

# The Chemistry and Literature of Beryllium

BY

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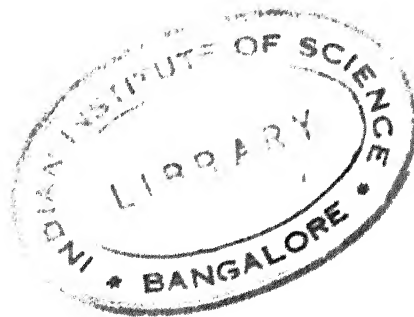
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## PREFACE.

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This book is written with the main object in view of saving preliminary study and labor to future investigators of beryllium and to point out some of the peculiarities of this interesting element which are apt to lead the novice toward erroneous conclusions. Especially is it desired to call attention to the fact that a large proportion of its accredited compounds are in reality but indefinite solid solutions. This condition of the literature of beryllium is due to the abnormal extent to which its hydroxide is soluble in solutions of its normal salts, giving rise to solids of almost any degree of basicity or to solutions with decreased osmotic effects. Accordingly, results of analysis, freezing points, etc., give little evidence of the true nature of its compounds, unless accompanied by proved definiteness of composition, a proof too often omitted throughout the whole field of inorganic chemistry, but nowhere more than in studying beryllium and its compounds.

More labor has been expended upon the bibliography than its limited extent may seem to indicate. It is believed that it will be found to contain references to all or nearly all the original articles on beryllium and that the references to abstracts will also be found fairly complete through 1902. Since 1902 the original articles and chief abstracts have alone been entered. It has been deemed advisable to include a brief abstract, at times critical in tone, of each article, but it is not claimed that these abstracts always cover the full subject matter of the original, although nothing important is intentionally omitted.

The Journals examined are approximately the same as those listed in James Lewis Howe's unexcelled Bibliography of the Platinum Metals and the plan followed is in general the same as outlined by him. The abbreviations used are familiar to all chemists.

Grateful acknowledgments are due especially to the libraries

of the Massachusetts Institute of Technology, the Library of Harvard University, the Boston Public Library and to the Library of the American Academy of Arts and Sciences. Also to the Boston Atheneum and to the libraries of Columbia University, N. Y., and the Surgeon General's Office and the Patent Office in Washington. The author also desires to express his thanks and appreciation of a grant allowed him by the American Association for the Advancement of Science toward expenses incurred in the preparation of the Bibliography.

CHARLES L. PARSONS.

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# PART I.

## CHAPTER I.

### INTRODUCTION.

**Discovery.**—In 1797 L. N. Vauquelin undertook to prove the chemical identity of the emerald and beryl, which had already been suspected by Haüy, and in the course of his analytical research, discovered that a portion of the precipitate which had previously been supposed to be aluminium hydroxide, was thrown out of its solution in potassium hydroxide on boiling. He also found that this new hydroxide was soluble in ammonium carbonate, formed no alum and was in many ways different from aluminum. These observations led him to announce in a paper read before the Institute on Feb. 14, 1898 (1798; 1),<sup>1</sup> the discovery of a new "earth."

**Name.**—In his first articles on the subject (1798; 1, 2 and 3), Vauquelin refers to the newly discovered oxide as "*la terre du Béril*," which was translated into German as "*Beryllerde*," from which the name Beryllium took its rise. At the end of Vauquelin's first article, the editors of the *Annales de Chimie* suggested the name "*glucine*," for the new oxide, and Vauquelin in his fourth publication (1798; 4) adopts the suggestion prefacing its use with the remark "*on a donné le nom de glucine*." As early as 1799, Link (1799; 3) had objected to the use of this term as too closely resembling "*glycine*," already in use, and indeed, Vauquelin, himself (1798; 3) seems to have accepted it with reluctance. In 1800 Klaproth (1800; 1) objected to its use because the salts of the yttrium earths were also sweet and Ekeberg (1802; 1) agrees with this idea. The name "*Beryllium*" itself was used when, in 1828, Wöhler, (1828; 2) for the first time, separated the metal. For the sake of uniformity in general usage which is overwhelmingly in favor of the name

<sup>1</sup> References are to Bibliography, Part II.

derived from beryl, and as "glucine" grew into use in French literature without being proposed by the discoverer, much as "beryllerde" in Germany, and for the reasons set forth in 1904, 11 and 1905, 2, it has been deemed advisable to adopt the name "Beryllium," already in use by far the majority of chemists.

**History.**—Following the discovery of the element, Vauquelin studied and announced the properties of some of its chief compounds. In 1828 the metal itself was produced in a very impure form by both Wöhler (1828; 2) and Bussy (1828; 3). Awdejew (1842; 2) added materially to the literature of the subject and made the first determinations of the atomic weight that have any claim to accuracy. Weeren (1854; 1) and Debray (1855; 1) also carried on extensive investigations of the metal, its atomic weight and chief compounds. Joy (1863; 1) undertook an extended research on the preparation of its compounds from beryl and published a fairly complete bibliography of the subject to his day. Atterberg and Nilson and Pettersson in the years between 1873 and 1885, made large additions to the chemistry of beryllium, and during these years a long, earnest and interesting discussion, which had begun as early as Awdejew's time, was carried on by Nilson and Pettersson, Humpidge, Reynolds, Hartley, Lothar Meyer, Brauner, and others regarding the valency of beryllium and its place in the periodic system. The discussion has continued up to the present day, but was in reality settled when Nilson and Pettersson (1884; 7, 8) determined the vapor density of the chloride, and Humpidge (1886; 1) showed that at high temperatures the specific heat of beryllium approached very closely to normal. Krüss and Moraht (1890; 4 and 5) made a re-determination of the atomic weight in 1890, and between the years 1895 and 1899, Lebeau published an important series of articles which are summed up by him (1899; 11) in one of the very best articles on beryllium and its compounds. Urbain and Lacombe (1901; 2) and Lacombe (1902; 3) discovered the remarkable basic salts of the acetic acid series and Parsons re-determined the atomic weight by new methods (1904; 5, 1905; 5) and studied many compounds, especially the so-called basic salts of some of the earlier writers (1904; 10, 1906; 1, 2,

3, 4, 13, 1907; 3, 10, 11). Numerous other investigators as will be seen from the bibliography, have also contributed to the chemistry of beryllium.

**Occurrence.**—The chief form in which beryllium is found in nature is the silicate, beryl,  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ , (BeO, 13.5 per cent.) including its gem forms, emerald and aqua marine and from this mineral most of the beryllium investigators have derived their material. Beryllium compounds have also been derived from gadolinite,  $\text{Be}_2\text{F}_3(\text{YO})_2(\text{SiO}_4)_2$ , (BeO, 10 per cent.) and leucophane,  $\text{Na}(\text{BeF})\text{Ca}(\text{SiO}_3)_2$ , (BeO, 10.3 per cent.). Other important minerals containing this element are chrysoberyl,  $\text{Be}(\text{AlO}_2)_2$ , (BeO, 19.2 per cent.); phenacite,  $\text{Be}_2\text{SiO}_4$ , (BeO, 45.5 per cent.); euclase,  $\text{Be}(\text{AlOH})\text{SiO}_4$ , (BeO, 17.3 per cent.); bertrandite,  $\text{H}_2\text{Be}_4\text{Si}_2\text{O}_9$ , (BeO, 42.1 per cent.); and eudidymite,  $\text{HNaBeSi}_3\text{O}_8$ , (BeO, 10.2 per cent.). Helvite, danalite, epididymite, crytolite, erdmanite, muromontite, alvite, foresite, arrhmitite, siphilitite, trimerite and meliphanite, are rare and complex silicates, while beryllonite,  $\text{NaBePO}_4$ , (BeO, 19.7 per cent.); herderite,  $(\text{CaF})\text{BePO}_4$ , (BeO, 15.4 per cent.); hambergite,  $\text{Be}_2(\text{OH})\text{BO}_3$ , (BeO, 53.3 per cent.), are interesting merely from a mineralogical standpoint as natural occurrence of the element. Beryllium has also been noted in some natural waters, in monazite sand, and in some aluminous schists. It is quite probable that it would have been found more frequently in rock analysis if some simple method of separating it from aluminum had been earlier known.

**Preparation from Beryl.**—Since beryl is not directly attacked by any acid, except, perhaps, by hydrofluoric when ground to a dust, it must first be fused with some flux or be heated in the electric furnace to a temperature (Lebeau, 1895; 5) which volatilizes some of the silica and leaves a residue easily attacked by hydrofluoric acid. For those having the facilities, this latter method presents many advantages. Among the fluxes which can be successfully used are sodium and potassium carbonates, calcium fluoride, potassium fluoride, calcium oxide, and sodium and potassium hydroxide. The fluorides possess the advantage in subsequent treatment, in the comparative ease of removal of the large

excess of silica, but for other reasons have been seldom used. Under average conditions the caustic alkalis, preferably potassium hydroxide, give the most satisfactory results.

Beryl is readily attacked by about its own weight of potassium hydroxide at a comparatively low heat in a silver or nickel crucible, although a salamandar or carborundum crucible can be used. Clay, graphite or iron crucibles are not available as they are immediately attacked. The fused mass should be broken up, just covered with water, strong sulphuric acid added until present in slight excess and the now gelatinous mass heated and broken up until fumes of sulphuric acid are given off and the whole has the appearance of a fine white powder. The residue is next treated with hot water when the sulphates of beryllium, aluminum, iron and potassium pass into solution and on evaporation most of the aluminum separates out as alum and can be removed. The mother liquors, containing all of the beryllium together with impurities, should be oxidized by boiling with nitric acid to convert the iron into the ferric condition, neutralized with ammonia and enough sodium bicarbonate crystals added to *saturate* the solution. The liquid should now be warmed and shaken frequently during a period of twenty-four hours, when most of the beryllium will pass into solution almost perfectly free from aluminum and also from iron unless other salts are present, which is sometimes the case. By again dissolving and re-treating the residue left after filtration, practically all the beryllium will be found in the bicarbonate solution. To this solution ammonium sulphide is added to remove any dissolved iron and the whole diluted to five times its original volume. By blowing steam through this solution to the boiling point the beryllium will be precipitated usually as a fine, granular basic carbonate easily filtered and washed. The basic carbonate will be found to be quite pure (1906; 2) save for some two per cent. of occluded sodium salt, but its  $\text{CO}_2$  content and the ease of filtration will vary greatly with the conditions of the hydrolysis and the length of the heating process. The method employed by Pollok (1904; 1) possesses some advantages in that he uses sodium hydroxide, dissolves in hydrochloric acid and after filtering off

the main part of the silica, without evaporation, passes hydrochloric acid gas through the filtrate, to the saturation point, whereby most of the aluminum is removed as the tetrahydrated chloride together with the remainder of the silica, and in a form which permits of easy washing. The beryllium may then be recovered, after oxidation of the iron, by its solubility in boiling acid sodium carbonate, in which the impurities ordinarily present are entirely insoluble, or it may be obtained in a less pure form by its solubility in ammonium carbonate, which is the method up to the present time almost universally employed.

The final separation by ammonium carbonate has the disadvantage that notable quantities of aluminum and iron also dissolve and the use, in large quantities, of a somewhat expensive reagent. It has the advantage of yielding the basic carbonate in a form which is easily washed from all impurities except ammonia. As is the case when acid sodium carbonate is used, solution takes place much more readily in the strongly saturated reagent, and the subsequent partial hydrolysis is greatly hastened by largely increasing the mass of the water present and is in both cases practically complete on diluting to a two per cent. solution and heating to the boiling point. Steam is much more preferable than direct heating as the violent and almost explosive "bumping" which is unavoidable in the latter case is thereby entirely prevented. Although not noted until very recently, (1906; 4) the basic carbonate produced in this manner contains about two and one-half per cent. of ammonia which can be removed by long boiling in pure water, which also gradually removes the carbon dioxide and leaves the beryllium in the form of the hydroxide, no more readily washed than if it had been precipitated as such. In practice a much better method is to heat the basic carbonate in contact with many times its weight of water, to momentary boiling with steam, filter and repeat several times with fresh water. This method is much more productive of results than washing with hot water, and the carbon dioxide is for the most part retained. The comparatively small amount of iron that dissolves in acid sodium or ammonium carbonate may be removed by adding ammonium sulphide, shaking and filtering off the fer-



rous sulphide with special precaution as to its oxidation during the filtration. The hydroxide or basic carbonate thus produced is the best form to use as a starting point in the production of other beryllium compounds.

Special purification from all other metallic elements can be most readily secured by conversion into the basic acetate and recrystallization from hot glacial acetic acid (1906; 1). On the other hand, the material prepared by the sodium bicarbonate method (1906; 2) is pure except for a small amount of sodium which can not be washed out. This can be removed by re-solution in acid and precipitation with ammonia.

Other methods for the removal of iron, aluminum, etc., will be noted under analysis.

#### SEPARATION AND DETERMINATION.

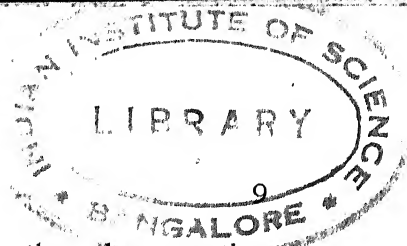
Except in the case of such pure salts as can be directly ignited to the oxide, beryllium is precipitated as the hydroxide, by ammonia or ammonium sulphide, washed with water to which a little ammonium acetate or nitrate has been added (1906; 2) and ignited to the oxide. When alone, its determination presents no difficulty except the great tendency of the hydroxide to pass through the filter in the colloidal state when washed with pure water. This is, however, entirely overcome by the use of ammonium acetate or nitrate as already noted.

**Detection.**—Follow the customary procedure of qualitative analysis until the sulphides insoluble in HCl have been removed. Concentrate the filtrate so obtained to 25 cubic centimeters and when cold add two grams solid  $\text{Na}_2\text{O}_2$ , boil and filter. Acidify the filtrate with  $\text{HNO}_3$  and add ammonia in excess. If no precipitate is obtained beryllium is absent. Wash any precipitate formed and add it together with two to three grams solid  $\text{NaHCO}_3$  to 20 cubic centimeters (10 per cent. solution) of water in a test-tube or casserole and bring rapidly to boiling. Boil for one-half minute only and filter to remove all aluminum. Dilute the filtrate with 10 volumes of water (one per cent. solution) and boil. Beryllium hydroxide containing a little carbonate will precipitate if present. Other elements do not interfere.

**Separation.**—In minerals and in admixture with other elements, the ordinary treatment—to separate aluminum and iron—should be followed and the beryllium will be found together with these two elements in their final separation. It is quite probable that beryllium has been weighed and calculated as aluminum in many mineral and rock analyses.

Many methods of separation of beryllium from iron and from aluminum, have been followed, although most reported analyses depend on the solubility of beryllium hydroxide in ammonium carbonate. Vauquelin (1798; 1) proposed the use of ammonium carbonate, but his first separation depended upon the solubility of beryllium hydroxide in potassium hydroxide and its precipitation on boiling. Gmelin (1840; 1) and Schaffgotsch (1840; 2) both used this same method, but it is very far from being accurate. Scheerer (1842; 3) first proposed the separation of the last traces of iron from the ammonium carbonate solution by means of ammonium sulphide. Berthier (1843; 2) suggested the use of ammonium sulphite as a reagent, but the method was shown to be valueless by Böttinger (1844; 1). In 1850, Rivot (1850; 1) proposed the ignition of the mixed oxides in a current of hydrogen, whereby the iron was reduced to metal and could be dissolved out with dilute nitric acid, or its mass determined by the loss in weight. Debray (1855; 1) developed a separation dependent upon the action of zinc on the mixed sulphates, precipitating the aluminum as a basic sulphate, but the method was never claimed to be quantitative. Joy (1863; 1) made a comparative study of all methods proposed to his time. Gibbs (1864; 3) first suggests the use of sodium fluoride, to quantitatively separate aluminum from beryllium, and Pollok (1904; 1) shows that the fluoride separation is exceedingly sharp. Cooke (1866; 1) after reducing the iron in hydrogen, volatilizes it in a current of hydrochloric acid gas. Havens and Way (1899; 5) accomplished the same result without previous reduction of the oxide. Rössler (1878; 9) succeeded in separating beryllium from small amounts of aluminum by precipitating with ammonium phosphate in presence of citric acid. Vincent (1880; 2) uses dimethylamine to precipitate beryllium salts and finds that the aluminum com-

pound is soluble in excess of the reagent; iron acts like beryllium. Renz (1903; 4) confirms this, states the same to be true of methyl, ethyl, and diethylamine and claims the results to be quantitatively accurate. Zimmermann (1887; 5) returns to the old potassium hydroxide method without any special addition. Schleier (1892; 6), Atkinson and Smith (1895; 9), and Burgass (1896; 7) separate iron quantitatively from beryllium by nitroso-beta-naphthol. Lebeau precipitates the iron in nitric acid solution with ferrocyanide, the excess of ferrocyanide with copper nitrate and the copper as sulphide. Hart (1895; 6) removes the major part of both iron and aluminum by careful precipitation of the sulphates with sodium carbonate, the beryllium being the last to precipitate, owing to the great solubility of its own hydroxide in its own sulphate. Havens (1897; 4) separates beryllium from aluminum quantitatively by the insolubility of aluminum chloride tetrahydrate in a mixture of hydrochloric acid and ether, which has been saturated with hydrochloric acid gas, and Pollok, (1904; 1) uses this same method for preparation purposes, omitting the ether. Wyrouboff (1902; 2) precipitates beryllium as the double oxalate with potassium from hydrochloric acid solution. Classen (1881; 3) electrolyzes in presence of oxalate of ammonium, the beryllium being dissolved in the carbonate of ammonium formed. Haber and Van Oordt (1904; 4) dissolve basic beryllium acetate in chloroform, leaving iron and aluminum acetates behind. Myers (1904; 7) removes iron electrolytically from a slightly acid solution of the sulphate, using a mercury cathode. Parsons and Robinson (1906; 1) separate basic beryllium acetate in a pure state from other acetates, by means of its ready solubility in hot glacial acetic acid and comparative insolubility in the same reagent when cold. Parsons and Barnes (1906; 2) show the solubility of beryllium hydroxide in a saturated solution of acid sodium carbonate, and the insolubility of the hydroxide of iron and aluminum in the same reagent. Glassmann (1906; 8) rediscovers the sulphite separation of Berthier (1843; 2), Böttinger (1844; 1) and Joy (1863; 1), and the fact that the method is old is pointed out by Friedheim (1906; 12), Noyes, Bray and Spear (1908; 2) give accurate methods for its separation and detection.



**Determination.**—In the opinion of the author, the separation by means of acid sodium carbonate offers the quickest, most direct and best method for estimating beryllium in admixture with other elements. The method of Havens (1897; 4) is equally accurate if care is taken to *fully saturate* with hydrochloric acid gas.

The first portion of the analysis will be the regular procedure, followed to obtain the hydroxides of iron and aluminum if present and the beryllium will be found also as an hydroxide in this precipitate. The mixed hydroxides of which less than one gram should be present, are dissolved in as little as possible hydrochloric acid, oxidized by a little nitric acid, ammonia added to nearly neutralize and evaporated to about 25 cubic centimeters. This solution is then heated to boiling and added with stirring to 75 cubic centimeters of hot (75°) water, containing 12 to 15 grams of the pure crystallized acid sodium carbonate. The beaker which contained the chloride is rinsed with a little hot water and the whole brought immediately to *boiling* and held there for one-half minute. Care must be taken not to confuse the evolution of carbon dioxide with the actual boiling of the liquid, which must take place. Under these conditions the beryllium hydroxide passes into solution, and the aluminum and ferric hydroxides are precipitated carrying with them a small amount of beryllium.<sup>1</sup> The liquid is allowed to cool and settle and is filtered into a liter beaker and washed three times with a hot (75°) solution of acid sodium carbonate containing 100 grams to the liter. The precipitate is now redissolved in hydrochloric acid and treated as before, allowing the filtrates and washings to run into the same beaker as first used. The filtrate is now carefully acidified with hydrochloric acid, the beaker being covered to prevent loss by spattering, is boiled to remove all carbon dioxide and the beryllium precipitated as hydroxide by ammonia, avoiding any large excess. The precipitate is allowed to settle, the supernatant liquid decanted through the filter and the precipitate washed twice with hot water, redissolved in a lit-

<sup>1</sup> Uranium may interfere as has been pointed out (1908; 2) but it is seldom present with beryllium and may be easily detected by ferrocyanide and its separation presents no difficulty.

tle hydrochloric acid and again precipitated with ammonia to remove sodium salts invariably occluded in the first precipitation. The precipitate is now washed with hot water containing two per cent. ammonium acetate or nitrate until the washings give no chlorine reaction. The hydroxide is ignited to the oxide in a platinum crucible without previous drying, and weighed.

## CHAPTER II.

### METALLIC BERYLLIUM.

**Preparation.**—Beryllium was first prepared in the elementary state by Wöhler (1828; 2) and by Bussy (1828; 3), acting independently, by the action of potassium on the anhydrous chloride. Davy (1809; 1) had previously attempted to reduce the oxide without success and Stromeyer (1812; 1) claimed to have reduced the oxide by a mixture of carbon, iron and linseed oil in 1812. Wöhler according to the records has priority over Bussy and deserves further credit in that he made a careful study of his product, which being very impure led him to announce some properties since shown to be erroneous. Debray (1855; 1) substituted sodium for potassium and passed his chloride, in the sublimed state, over the melted metal. Menier (1867; 1) exhibited a sample of metallic beryllium at the Paris Exposition, which he had prepared by the action of sodium upon a mixture of beryllium chloride and the double fluorides of beryllium and potassium in a crucible of pure aluminum. Reynolds (1876; 3) reduced the chloride by sodium, and Nilson and Pettersson (1878; 3 and 4) used the same method and succeeded in obtaining a metal of 87 per cent. purity by fusing under a salt cover in a crucible of iron tightly closed. Again (1880; 6 and 7) the same authors succeeded in procuring a metal of 94 per cent. purity but it was not until Humpidge (1885; 1, 1886; 1) made his final specific heat determinations in 1885, that a metal of as high a degree of purity as 99.2 per cent. was obtained. Winkler (1890; 3) claimed to have reduced the oxide by magnesium and Goldsmith (1898; 14) by aluminum, but both chemists were undoubtedly mistaken. Krüss and Moraht (1890; 4 and 5) reduced the double fluoride of beryllium and potassium with sodium, obtaining their metal in hexagonal plates. Pollok (1904; 1 and 9) again produced the metal by decomposition of the chloride with sodium, and states that he was unable to fuse to-

gether the dark gray powder formed for the reason that it probably volatilizes at ordinary temperatures without passing through the liquid condition.

It was left to Lebeau (1898; 3) to develop an apparently simple and easy method for producing the metal almost free from admixture, which he did by electrolyzing the double fluoride of beryllium and of potassium or of sodium in a nickel crucible. It is true that Warren (1895; 10) had claimed to *manufacture* the metal by the electrolysis of the bromide which does not conduct electricity, and Borchers (1895; 11) had proposed the preparation by means of electrolyzing the chloride, mixed with an alkali chloride but apparently without result. Lebeau proved that the halides of beryllium did not conduct electricity so he added sodium fluoride to beryllium fluoride, melted the mass in a nickel crucible which itself became the cathode, and using a carbon anode, passed a current from a dynamo yielding normally 20 amperes at 80 volts. Care was exercised to keep the heat but little above the melting point and metal was obtained in hexagonal crystals.

Some patents of Liebermann (1898; 15 and 16) and Kühne (1907; 2) for the production of beryllium would appear to be of very doubtful value.

**Physical Properties.**—Beryllium is a hard, dark steel gray metal, which especially in its crystal form has a bright metallic luster. The crystals produced by electrolysis (Lebeau, 1898; 3, 1899; 11) are hexagonal lamellae, placed one on the other and according to Brögger and Flink (1884; 4) occur in two forms, prismatic and tabular, belonging to the holohedral division of the hexagonal system and having an axis relation of  $a:c=1:1.5802$ .

The *specific gravity* of the crystals is 1.73 at 15° (Lebeau, 1899; 11), of the metal produced by reduction with sodium 1.85 at 20° (Humpidge, 1886; 1). Other published figures were on impure material and need not be given.

The *melting point* is not known for at ordinary pressures and in an inert atmosphere it volatilizes without fusion, (Pollok; 1904; 1). Under pressure it can be fused (Nilson and Petters-

son, 1878; 3) but no determinations of the temperature have been made.

The *specific heat* at ordinary temperatures is abnormal as in the case of boron, carbon and silicon, but Humpidge (1885; 1, 1886; 1) has shown that between 400° and 500° it remains practically constant at about 0.62. The matter was one of long controversy and the low results obtained by Nilson and Pettersson (1878; 3) and others was the chief cause of the belief in the trivalency of beryllium. According to Humpidge (1885; 1 and 6, 1886; 1) the relation between specific heat and temperatures can be expressed by the empirical formula:

$$K_t = 0.3756 + 0.00106 t - 0.00000114 t^2.$$

According to Thalén (1869; 2) who was first to study the *spectra* of beryllium it is characterized by a line 4572.0 in the blue and 4488.5 in the indigo of about equal intensity. Lockyer (1878; 10) finds beryllium lines in the sun's spectra. Hartley (1883; 5) makes a careful study of the arc spectra of the chloride and publishes a chart of the spectra of beryllium, which besides the two lines in the visible spectra noted above by Thalén, he finds the lines 3320.5, 3130.2, 2649.4, 2493.2, 2477.7 of which 3130.2 is the strongest and most persistent. Rowland and Tannall (1895; 4) in their exhaustive study of the arc spectra of the elements, found the most prominent lines for beryllium between 2100 and 4600 to be

2348.697	2650.414	3321.218
2350.855	2651.042	3321.486
2494.532	3130.556	4572.869
2494.960	3131.200	

These observations were made with a grating of 21½ feet radius and 20,000 lines to the inch on a photographic plate 19 inches in length and are unsurpassed for accuracy. Formánek (1900; 3) finds that the chloride treated with Alkanna tincture presents a strong orange red fluorescence and yields three absorption bands. Soret (1878; 11) finds that solutions of the chloride give no absorption spectra and only a feeble bluish fluorescence. Crookes (1881; 4) found that beryllium oxide, in high vacuo, gave a beautiful blue phosphorescence, but

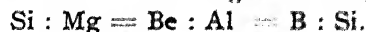
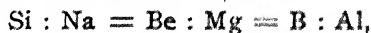


no spectral rays. Hartley (1901; 1) finds that the lines  $\lambda$  3130.3 and 2478.1 are still visible in solutions of beryllium salts when the concentration has fallen so low as 0.000001 per cent.

The *atomic weight* of beryllium is very close to 9.1. The first determination was made by Berzelius (1815; 1) early in the last century and were little more than approximations. The corrected results of other investigators with the ratio determined are as follows:

		Mean O = 16
Awdejew (1842; 2)	BeO : BaSO <sub>4</sub> . . . . .	9.34
Weeren (1854; 1)	BeO : BaSO <sub>4</sub> . . . . .	9.27
Debray (1855; 1)	BeO : 4CO <sub>2</sub> . . . . .	9.34
Klatzo (1869; 1)	BeO : BaSO <sub>4</sub> . . . . .	9.28
Nilson and Pettersson (1880; 6)	BeSO <sub>4</sub> ·4H <sub>2</sub> O : BeO .	9.104
Krüss and Morahit (1890; 5)	BeSO <sub>4</sub> ·4H <sub>2</sub> O : BeO .	9.05
Parsons (1904; 5)	{ Be(C <sub>2</sub> H <sub>7</sub> O <sub>2</sub> ) <sub>2</sub> : BeO .	9.113
	{ Be <sub>4</sub> O(C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sub>6</sub> : BeO	9.113
Parsons (1905; 5)	{ Algebraic combina- tion of above. Be and C unknown	9.112

**Chemical Properties.**—Chemically, beryllium is a metal slightly less basic in its nature than magnesium. According to Brauner (1881; 1) the chemical nature of beryllium may be summed up by the three statements:



Beryllium is not altered in dry air nor in oxygen at ordinary temperatures but takes fire when highly heated and if finely divided yields bright sparks in the flame of a Bunsen burner. (Lebeau, 1899; 11). It combines directly and easily with fluorine, chlorine and bromine (Lebeau, 1898; 3) and with iodine when heated in its vapor (Wöhler, 1828; 2) and (Debray, 1855; 1). Wöhler claimed to make a sulphide by heating in sulphur vapor but Fremy, (1853; 1) and Debray, (1855; 1) were unable to get the two elements to combine directly and it has not since been produced in this manner. Strong sulphuric acid attacks beryllium, giving off sulphur dioxide. Hydrochloric acid and dilute sulphuric acid as well as solutions of the caustic alkalies

attack the metal with evolution of hydrogen. The gaseous hydracids attack it violently if passed over the heated metal. Strong nitric acid has little effect upon the metal but weaker acid attacks it giving off nitric oxide. It is but little acted upon by cold water, but is slowly converted into the hydroxide by boiling water.

Beryllium acts upon methyl and ethyl iodides, (Cahours, 1860; 1) replacing the iodine and forming beryllium ethyl and beryllium methyl. It also replaces mercury in its analogous compound and in mercury propyl, (Cahours, 1873; 1, Lawroff, 1884; 3).

Wöhler (1828; 2) thought he had prepared the selenide, telluride, arsenide and phosphide by fusing with the respective elements but his observations have not been confirmed. Beryllium has probably never been obtained in combination with hydrogen although Winkler, (1891; 3) thought he had produced a hydride. Beryllium unites directly with carbon, boron and silicon at the heat of the electric furnace (Lebeau, 1895; 2, 1898; 7, 1899; 11). It reduces  $\text{SiCl}_4$  when heated, (Rauter, 1892; 2).

**Valency.**—The valency of beryllium was long in doubt and gave rise to an animated discussion extending over many years and calling forth much research. The question was in reality settled when Nilson and Pettersson, (1884; 7) and (1885; 3), against all their previous contentions, found the vapor density of beryllium chloride to be entirely in accord with the divalency of the metal. Their determinations were made between 490 and 1520° C, and above 1000°, their results are quite constant for the formula  $\text{BeCl}_2$ . The divalency was confirmed by Humpidge by the specific heat at high temperatures and by the vapor density of both chloride and bromide, (1886; 1), by Coombes, (1894; 6) by the vapor density of the acetylacetonate, and by Urbain and Lacombe, (1901; 2) by the vapor density of the basic acetate. Rosenheim and Woge (1897; 4) also found the formula for the chloride to be  $\text{BeCl}_2$  by the rise of the boiling point of its solution in pyridine.

**Alloys of Beryllium.**—Our knowledge of the alloys of beryllium is confined solely to the work of Lebeau (1897; 8, 1898;

4, 1899; 11) and, although he produced alloys with the common metals and Cr, Mo and W, he describes those of copper only. His alloys were made either by heating the mixed oxides of beryllium and the metal to be alloyed with an intimate mixture of carbon to a very high temperature in the electric furnace, or they are produced simultaneously with the electrolytic production of beryllium, by substituting a graphite for the nickel crucible and fusing in this the metal to be alloyed, while the double fluoride of beryllium and sodium was being electrolyzed in the same crucible. Alloys of about 10 per cent. Be to 90 per cent. Cu are pale yellow, nearly white. Alloys of 5 per cent. Be are yellow, easily polished and malleable, cold or hot. They are not oxidized in the air, but are tarnished by hydrogen sulphide. They are dissolved by nitric acid with difficulty. As little as 0.5 per cent. of beryllium changes very noticeably the appearance of the copper and makes it decidedly sonorous. An alloy containing 1.32 per cent. of beryllium has the color of gold and is very sonorous. It is easily polished and can be readily forged.

## CHAPTER III.

### NORMAL COMPOUNDS OF BERYLLIUM.

All normal compounds of beryllium which are soluble in water are strongly acid in reaction to litmus, dissolve notable quantities of their own hydroxide which increases in amount with the concentration of the solution, set free carbon dioxide from carbonates and attack certain metals. In short, they act in many respects like the acids themselves would act from which they are derived. In spite of these facts they show less hydrolysis, and consequent smaller concentration of hydrogen ions, at least in the case of the chloride, nitrate and sulphate, (Leys, 1899; 10 and Brunner, 1900; 1) when treated by the well-known method of sugar inversion, than the corresponding salts of iron and aluminum. By the same method of determination, the hydrogen ions are thrown back into the undissociated condition when but a small fraction of the beryllium hydroxide has been dissolved which the normal salt is capable of holding in solution, (Parsons, 1904; 10). The reasons for these phenomena are not at present understood. The sulphate has been recently studied with a view to a solution of this problem, (1907; 10) and it has been shown that the addition of beryllium hydroxide to a solution of the sulphate, raises the freezing point and diminishes the conductivity; that no beryllium enters into the formation of a complex anion and that while the hydroxide can be partially removed by dialysis if dialyzed into pure water, there is little evidence of a colloid being present. It has been suggested that we may have here a new instance of solution, wherein the solid, when once dissolved, acts as a true solvent for its own oxide or hydroxide, and there are some analogies which point strongly to this view, (1907; 11).

To this same cause, whatever it may be, is due the fact that no normal carbonate or nitrite is known, and that the chloride, bromide, iodide and nitrate lose their anion so readily when in contact with water that they can only be prepared with

special precaution against hydrolysis and solution of the hydroxide formed.

### BERYLLIUM HALIDES.

The halides of beryllium, with the exception of the chloride, were little known until Lebeau gave them most careful study. They are, excepting the fluoride, only prepared pure in the absence of all water. By careful evaporation of the fluoride in the presence of ammonium fluoride or in an atmosphere of hydrofluoric acid gas, it can apparently be kept from hydrolytic action, (Lebeau, 1899; 11) but this is not true of any of the other halides. On evaporating their solutions in water they lose more or less of the gaseous hydracids, the residue becoming more and more basic and remaining soluble until a surprising degree of basicity is reached. This hydrolytic action is comparatively small in the case of the fluoride, but is practically complete in the case of the chloride, bromide and iodide. By careful manipulation residues of almost any degree of basicity can be obtained and these mixtures of base and normal salt have given rise to claims for numerous *oxyfluorides* and *oxychlorides* for the existence of which there is no other evidence than the analysis of the variable residues obtained.

**Beryllium Fluoride,  $\text{BeF}_2$ .**—The first experiments on the relation of fluorine to beryllium were made by Gay Lussac and Thenard in 1811 (1811; 1). Later in 1823, Berzelius (1823; 1) made the fluoride by dissolving the oxide in hydrofluoric acid and described the properties of the solution so produced and the residue left on evaporation, the basic nature of which he recognized. Klatzo (1869; 1) made a short study of the fluoride, but the pure salt was not produced until Lebeau (1898; 8, 1899; 11) made it by heating the double fluoride of ammonium and beryllium, which had previously been dried over phosphoric anhydride, in a current of dry carbon dioxide and cooled in an atmosphere of the same gas. He also prepared it by the action of hydrofluoric acid gas on the carbide.

**Properties.**—According to Lebeau the pure fluoride is a glassy, transparent mass having a specific gravity of 2.01 at 15°. It

becomes fluid towards  $800^{\circ}$ , passing through a viscous condition, but above  $800^{\circ}$  it begins to volatilize, yielding white and very deliquescent crystals. It dissolves in all proportions in water, is only slightly soluble in absolute alcohol, but dissolves readily in 90 per cent. alcohol. By cooling an alcoholic solution to  $-23^{\circ}$ , one obtains a white crystalline mass which, however, melts easily on rise of temperature. It is also soluble in a mixture of ether and alcohol. The majority of metalloids are without action on the fluoride. It is insoluble in anhydrous hydrofluoric acid and is not altered by it, rendering the existence of an acid salt quite improbable. It is readily attacked by sulphuric acid. The alkali metals and magnesium reduce it, but the difficulty of fusion and hygroscopicity renders the preparation of pure metal difficult. With potassium the reaction begins below  $500^{\circ}$ . Lithium and magnesium act at about  $650^{\circ}$ . Aluminum fuses without alteration.

**Beryllium Chloride,  $\text{BeCl}_2$ .**—Although Vauquelin (1798; 5) obtained the chloride in solution, the pure salt was not made until Rose (1827; 1) prepared it in the sublimed anhydrous state by passing chlorine gas over a heated mixture of carbon and beryllium oxide. Wöhler (1828; 2), Awdejew (1842; 2), Debray (1855; 1), Klatzo (1869; 1), Nilson and Pettersson (1880; 6, 7, and 8, 1885; 3), Pollok (1904; 12) and others used the same method of preparation. Nilson and Pettersson (1885; 3) prepared the chloride in very pure form for the purpose of determining its vapor density by the action of dry hydrochloric acid gas on the metal. Lebeau (1895; 2, 1899; 11) utilized the carbide which is readily attacked when heated by both chlorine and gaseous hydrochloric acid. Lothar Meyer (1887; 1) obtained the chloride by passing carbon tetrachloride vapor over heated beryllium oxide. Bourion (1907; 7) prepares the chloride by the action of a stream of mixed Cl and  $\text{S}_2\text{Cl}_2$  on the oxide at a red heat. No matter what method is used the materials must be absolutely dry if a pure chloride is to be obtained. Awdejew (1842; 2) and Atterberg (1873; 7) thought they had produced a hydrous chloride,  $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ , by evaporating the chloride slowly over sulphuric acid, but Parsons (1904; 5) shows that the procedure recom-

mended invariably yields basic mixtures of varying degrees of hydration. Atterberg's results are easily explained when one considers that his formula depended solely on an analysis for chlorine alone, and although Awdejew gives no details of his analytical results, it is probable he was led to his undoubtedly erroneous conclusion in the same way.

**Properties.**—The anhydrous chloride is a white crystalline solid having a melting point about  $440^{\circ}$  (Lebeau, 1899; 11. Pollok, 1904; 12). Carnalley (1879; 1, 1880; 1, 1884; 9, 1884; 10) obtained much higher figures, but was certainly in error. The boiling point is about  $520^{\circ}$  as shown by Nilson and Pettersson and confirmed by Pollok (1904; 1). Its vapor density first determined by Nilson and Pettersson (1884; 7, 1885; 3) between  $490^{\circ}$  and  $1520^{\circ}$ , is in entire accord with the formula  $\text{BeCl}_2$ . This was confirmed by Humpidge (1886; 1). Rosenheim and Woge (1897; 4) showed that the molecular weight as determined by the raising of the boiling point of a solution of beryllium chloride in pyridine, was in agreement with the same formula. Its molecular heat of solution is  $44.5\text{K}^{\circ}$  and its molecular heat of formation is  $155\text{K}^{\circ}$  (Pollok, 1904; 9). Its magnetic susceptibility was determined by Meyer (1899; 3). The fused chloride does not conduct the electric current, (Lebeau) but its alcoholic solution is a conductor (Pollok, 1904; 1).

Beryllium chloride dissolves in water with great avidity and, unless special precautions are taken, with loss of chlorine as hydrochloric acid. On evaporation the solution loses hydrochloric acid more or less readily according to conditions, and the residue left, which may be of almost any degree of basicity, has been mistaken for an oxychloride by Atterberg (1873; 7, 1875; 4). With ether it forms the compound  $\text{BeCl}_2 \cdot 2[(\text{C}_2\text{H}_5)_2\text{O}]$ . (Atterberg, 1875; 4). It also forms a white crystalline compound containing the chloride with both hydrochloric acid and ether (Parsons, 1904; 5), the exact composition of which has not been determined.\* It is also readily soluble in alcohol, and yields a crystalline compound with it, but is almost insoluble in benzene, chloroform, carbon tetrachloride and sulphur dichlo-

\* Since this went to press a letter from H. Steinmetz informs me that these crystals are in reality  $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ . It is accordingly certain from the conditions that this compound was never made by Atterberg. Its identification belongs to Steinmetz. My incorrect observation was qualitative only and made in the course of another investigation.

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ride (Lebeau, 1899; 11). It combines with ammonia gas and with phosphine. Lebeau (1899; 11) claims that it forms many crystalline compounds with the organic bases, but Renz (1903; 3) was only able to obtain the compound,  $\text{BeCl}_2 \cdot (\text{C}_9\text{H}_7\text{N}_2)_2 + \text{H}_2\text{O}$ , with quinoline. By experiments on the chloride and sulphate, Höber and Kieson (1898; 9) were able to show that their taste was due to the cation. The chloride forms many double salts (vidi, Double Salts). According to Brunner (1900; 1) and Leys (1899; 10), beryllium chloride solutions are less hydrolyzed than those of aluminum and iron, although about two per cent. of the molecules are so decomposed. Awdejew (1842; 2) and Nilson and Pettersson (1884; 7, 1885; 3) claim that the sublimed chloride attacks glass, but Parsons (1904; 5) states that this is probably incorrect.

**Beryllium Bromide.**—The bromide was first prepared by Wöhler (1828; 2) by the action of bromine vapor on the metal and also upon a mixture of carbon and beryllium oxide. Berthelot (1831; 1) obtained it in solution by dissolving the oxide in hydrobromic acid. Humpidge (1883; 7) also prepared it by acting on a mixture of the oxide and carbon with dry bromine. Lebeau (1899; 11) prepared it by the action of bromine and gaseous hydrobromic acid on the carbide.

**Properties.**—The anhydrous bromide is obtained always by sublimation and in colorless white crystals. Its vapor density determined by Humpidge (1886; 1) is in accord with the formula  $\text{BeBr}_2$ . Its melting point was determined by Carnalley and Williams (1879; 1, 1880; 1, 1884; 9 and 10) but the values obtained were much too high, as shown by Lebeau (1899; 11), who states that it fuses at about  $490^\circ$  and begins to sublime somewhat below this temperature. The fused salt does not conduct electricity, although Warren (1895; 10) claimed to make the metal in some quantity by electrolyzing it. For a knowledge of its chemical properties we are indebted almost wholly to Lebeau (1899; 11) who states that it acts much the same as the chloride. It dissolves in water with avidity, losing hydrobromic acid on evaporation. It is soluble in absolute alcohol



and forms a crystalline compound therewith. It combines with ammonia and with the organic bases.

**Beryllium Iodide**,  $\text{BeI}_2$ .—Wöhler (1828; 2) and Debray (1855; 1) prepared the iodide by the action of iodine upon the metal, but we are indebted almost solely to Lebeau (1898; 6, 1899; 11), who prepared it in some quantity by the action of gaseous hydriodic acid, or a mixture of hydrogen and iodine vapor, on the carbide at about  $700^\circ$ , for a knowledge of its properties.

**Properties**.—According to Lebeau (1899; 11), beryllium iodide, as obtained in the sublimed state, consists of colorless crystals, which are quickly decomposed in moist air. Their specific gravity at  $15^\circ$  is close to 4.20. They begin to sublime below their melting point which is  $510^\circ$ . The melted iodide boils between  $585^\circ$  and  $595^\circ$ . It is insoluble in benzene, toluene, spirits of turpentine, and but slightly soluble in carbon disulphide. The slightest trace of water attacks it immediately, but it is not quite so sensitive after fusion, probably because less surface is exposed. It can be distilled without alteration in dry hydrogen, nitrogen or carbon dioxide. Its iodine is readily replaced by chlorine or bromine. Fluorine forms fluorides of both beryllium and of iodine. Fluorine and chlorine both attack it even when cold, giving off heat and light. Cyanogen acts upon it at about a red heat, producing a white material, less volatile than the iodide, which with water gives a clear solution reacting for cyanides. Heated in oxygen, it takes fire at about a red heat and the vapor itself will burn even in air. Heated with sulphur it yields a sulphide of beryllium, readily decomposed by water. The vapor of phosphorus also attacks it, probably forming a phosphide of beryllium. Sodium, potassium and lithium reduce it at about  $350^\circ$ . Magnesium reduces it at about  $450^\circ$ . Aluminum, silver, copper and mercury are without action below the temperature of the softening of glass. Hydrogen sulphide acts upon it, but only at elevated temperatures and yields a white sulphide. It absorbs large amounts of ammonia gas and forms compounds which melt easily and can be crystallized on cooling. It reacts with a large number of organic compounds. It is soluble in alcohol and pro-

duces a crystalline compound therewith. It also combines with ether. It differs from the iodide of aluminum in not reacting with cold tetrachloride of carbon. It also does not act upon  $C_2Cl_4$ . Acetic anhydride and anhydrous chloral give energetic reactions with beryllium iodide. Ammonium compounds and organic bases, especially aniline and pyridine, produce crystalline compounds with it.

#### BERYLLIUM OXIDE.

**Preparation.**—The oxide is prepared by heating the nitrate, sulphate, oxalate, hydroxide, basic carbonate or other salt of beryllium containing a volatile acid radical, and even the chloride, bromide and iodide yield practically all of their metal as oxide when evaporated from solution and heated. By evaporating to dryness a mixed solution of beryllium chloride and ammonium chloride and heating in air, an oxide so light and feathery is produced that it is difficult to retain it in the containing vessel.

**Properties.**—The oxide is a white powder as ordinarily produced which can be volatilized and crystallized at high temperature. According to Levi-Malvano (1905; 7) a blue oxide is obtained by igniting the hexahydrated sulphate (vidi sulphates).<sup>1</sup> In the electric furnace, (Lebeau, 1896; 6, 1899; 11) it can be fused and even volatilized and yields a crystalline mass slightly harder than corundum. The crystals are hexagonal (Lebeau, 1899; 11). Mallard, (1887; 4) states that they are positive and uniaxial and he measured parameters  $a:h=1:1.6305$ . He further states they are isomorphous with zinc oxide, and Ebelmen (1851; 1) states that they are isomorphous with aluminum oxide. The oxide is diamagnetic (Nilson and Pettersson, 1880; 9) and its magnetic susceptibility has been determined by Meyer (1899; 3).

The *specific gravity* was first determined by Ekeberg (1802; 1) as 2.967. Rose (1848; 2) found 3.021 to 3.09, claiming the lower figure was obtained by high heating. Ebelmen (1851; 1) reported 3.058; Nilson and Pettersson (1880; 9, 1880; 10) ob-

<sup>1</sup> Repeated attempts by the author of this book to reproduce this oxide or even the hexahydrated sulphate have met with failure.

tained 3.016 and Grandeau (1886; 2) 3.18. Later results on very pure material gave Krüss and Moraht (1890; 7) 2.9644; Lebeau (1896; 6, 1899; 11) at 0°, 3.01-3.025; Parsons (1904; 5) at 4°, 2.9640. According to Lebeau, fusing the oxide had very little effect on the specific gravity.

The *specific heat* of beryllium oxide is 0.247 between 0° and 100° (Nilson and Pettersson, 1880; 9 and 10). According to Tanatar it is 0.2898 between 100-117°.

Crystals of the oxide have been produced by melting in the electric furnace (Lebeau, 1896; 6), by fusing a mixture of beryllium silicate and potassium carbonate (Ebelmen, 1851; 1), by fusing a mixture of sulphate of potassium and sulphate of beryllium (Debray, 1855; 1), by fusing a mixture of sulphate of potassium and phosphate of beryllium (Grandeau, 1886; 2), by dissolving the oxide in fused beryllium leucite (Hautefeuille and Perrey, 1890; 9) and by fusing the sulphate with silicic acid (Hautefeuille and Perrey, 1890; 14).

Beryllium oxide is not reduced by hydrogen, magnesium, sodium, potassium or aluminum (Lebeau, 1896; 6, 1899; 11). According to Franck (1898; 20), aluminum does form alloys at high temperature by heating with beryllium oxide. It is reduced by carbon at high temperatures in the presence of other metals, such as copper, forming alloys therewith, or, when treated alone at high temperatures with either carbon, boron or silicon it is reduced, forming the carbide, borocarbide or silicide (Lebeau, 1899; 11). It is not acted upon by water or carbon dioxide. Ballard (1834; 1) states that bromine water, especially under the influence of sunlight partly dissolves beryllium oxide, but Lebeau (1899; 11) finds that it is not affected by bromine, chlorine, iodine or others of the non-metals except fluorine, which attacks it directly with the formation of a fluoride. Mixed with carbon and heated in a current of a halogen gas the corresponding halide is formed and Meyer (1887; 1) found that the anhydrous chloride was formed if the oxide was heated in a current of carbon tetrachloride vapor. Bourion (1907; 7) found that it was also acted upon by  $S_2Cl_2$  at a red heat with the formation of the chloride.

The gaseous hydracids have no action on the oxide, even at high temperatures. Strong hydrochloric and nitric acids dissolve the oxide slowly. Strong sulphuric acid attacks it readily forming the anhydrous sulphate which dissolves only slowly on dilution with water as hydration progresses. Rose (1848; 3, 1855; 2) states that beryllium oxide partially decomposes solutions of  $\text{NH}_4\text{Cl}$ , but loses this property if heated. Atterberg (1873; 7) states that the oxide is not soluble in fused potassium hydroxide. According to Ebelmen (1851; 1), it is readily soluble in potassium bisulphate.

**Beryllium Sulphide.**—Wöhler (1828; 2) supposed he had made a sulphide by heating the metal with sulphur, but Fremy (1853; 1) states that it was the only sulphide he could not produce by passing the vapor of carbon disulphide over the hot oxide. Debray (1855; 1) and Nilson and Pettersson (1873; 3) state that beryllium and sulphur do not combine when heated together. Berzelius (1826; 2) supposed he produced a double sulphide of beryllium and tungsten, but his results lack confirmation. Lebeau (1899; 11) at last made the sulphide by heating the anhydrous chloride and iodide with sulphur or with hydrogen sulphide. Also by the action of sulphur vapor on the carbide at a high temperature. The sulphide is a white solid, immediately decomposed by water. No other details are given nor further study of this compound been made.

**Beryllium Selenide, Beryllium Telluride.**—Preparation claimed by Wöhler (1828; 2), but probably he was mistaken.

**Beryllium Trinitride.**—Attempts to make the trinitride (Curtius and Rissom, 1898; 12) by the action of a solution of beryllium sulphate on barium trinitride failed, as it immediately broke down to beryllium hydroxide and hydronitric acid.

**Beryllium Phosphide.**—Claimed by Wöhler (1828; 2), by the action of phosphorus on the metal, but unconfirmed by this method. Lebeau, however, (1899; 11) prepared a compound of beryllium and phosphorus, which he did not analyze or describe, by means of the action of phosphorus vapor on anhydrous beryllium chloride and iodide.

**Beryllium Cyanide.**—By the action of cyanogen gas on beryllium iodide, Lebeau (1898; 6, 1899; 11) produced a cyanide compound of beryllium which he neither studied nor analyzed.

**Beryllium Carbide,  $\text{Be}_2\text{C}$ .**—The carbide of beryllium has been produced by Lebeau (1895; 2, 1899; 11) by heating a mixture of one part carbon and two parts beryllium oxide in an electric furnace, using a current of 950 amperes and 50 volts for about ten minutes. Lebeau first gave it the formula  $\text{Be}_4\text{C}_3$ , but after Henry (1895; 8) called his attention to his error, he adopted the formula  $\text{Be}_2\text{C}$ . Its properties are quite similar to those of aluminum carbide. At  $15^\circ$  its specific gravity is 1.9. It is so hard it scratches quartz easily. It consists of yellowish brown transparent crystals. Fluorine, chlorine and bromine attack it readily if heated, forming the corresponding halide and leaving a residue of carbon. Iodine is without action at  $800^\circ$ . Oxygen attacks it only superficially when heated. The vapor of sulphur reacts at about  $1000^\circ$ , forming the sulphide. Hydrofluoric acid gas attacks it at about  $450^\circ$ , forming the fluoride. Hydrochloric acid gas forms the chloride at about  $600^\circ$  and sets free carbon and hydrogen. Hydriodic acid gas attacks it at about  $750^\circ$ , yielding the iodide. Beryllium carbide slowly decomposes water yielding beryllium hydroxide and pure methane. The reaction is much more rapid in solution of potassium hydroxide. The carbide reduces concentrated sulphuric acid, although it is but slowly attacked by concentrated nitric and hydrochloric acids. These same acids diluted dissolve it completely after a few hours. Fused potash attacks it with incandescence and it is oxidized by potassium permanganate and peroxide of lead. The chlorate and nitrate of potassium do not attack it.

**Beryllium Borocarbide,  $3\text{Be}_2\text{C}.\text{B}_2\text{C}_3$ .**—By heating a mixture of boron and beryllium oxide in a carbon tube by means of a current of 150 amperes and 45 volts, Lebeau (1898; 7, 1899; 11) produced some bright metallic crystals to which he gave the formula  $\text{Be}_6\text{B}_4\text{C}_4$ . The borocarbide has a specific gravity of 2.4 at  $15^\circ$ . It is not altered in air unless heated and then oxidizes only superficially. Fluorine, chlorine, bromine and iodine, as well as their hydracids, act much the same as on the pure carbide. Sulphur

attacks it only superficially at a red heat. Mineral acids and especially nitric acid dissolve it rapidly.

**Beryllium Silicide.**—Lebeau (1899; 11) also obtained a silicide of beryllium, but was unable to purify it sufficiently to determine its properties or formula.

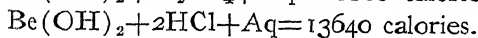
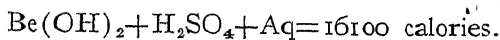
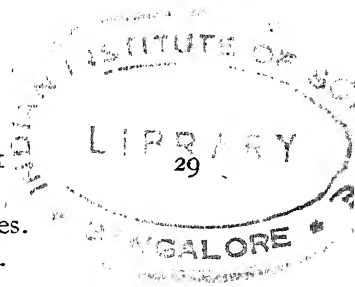
**Beryllium Hydroxide,  $\text{Be}(\text{OH})_2$ .**—Beryllium hydroxide is a white gelatinous mass physically indistinguishable from aluminum hydroxide and resembling it very closely from a chemical standpoint. It is precipitated from solutions of beryllium salts by ammonia, ammonium sulphide, caustic alkalies and barium carbonate. It is also precipitated by methyl, dimethyl, ethyl, and diethyl amines (Vincent, 1880; 2, Renz, 1903; 4). Soluble normal carbonates throw down a basic mass which consists largely of the hydroxide together with some carbonate. The latter may, however, be almost entirely eliminated by boiling. It is readily attacked by solutions of acids. It dissolves slowly in concentrated solutions of ammonium carbonate (Vauquelin, 1798; 1, et al.) and sodium bicarbonate. It is immediately soluble in a saturated boiling solution of sodium bicarbonate (Parsons and Barnes, 1906; 2). It is, however, almost insoluble in a dilute solution and a strong solution which has dissolved the hydroxide, on dilution (two per cent. or less  $\text{NaHCO}_3$ ) slowly hydrolyzes in the cold and throws out the basic carbonate or does so immediately on boiling. It is almost insoluble in normal sodium carbonate. It is soluble in sodium and potassium hydroxides forming beryllonates which are hydrolytically decomposed on boiling. This decomposition is complete if excess of base is not present, but may be partially or entirely prevented by increasing the mass of the soluble hydroxide. It is soluble in solutions of its own salts and in proportion to the concentration of the particular salt used. From concentrated solution in its own salts, it is precipitated by dilution, but such precipitation is never complete. It is insoluble in excess of ammonium sulphide, ammonia, and methyl, ethyl, dimethyl and diethyl amines (Vincent, 1880; 2, Renz, 1903; 4). When washed with pure water it slowly passes through the filter in colloidal solution (Parsons and Barnes, 1906; 2). Beryl-

lium hydroxide, like aluminum hydroxide, is more susceptible to reaction when freshly precipitated (Haber and Van Oordt, 1904; 2). This is more especially apparent in the case of carbon dioxide, for when freshly precipitated it will absorb about one third of an equivalent of this gas, but if allowed to stand sometime and especially if first heated, it almost entirely loses this property (Parsons and Roberts, 1906; 4). Leys (1899; 10) states that it is 11 times as basic as aluminum hydroxide. It has, like most other gelatinous hydroxides, a very great tendency to occlude other substances which may be present when it is precipitated and it is almost impossible to remove these substances by washing. It is nearly insoluble in water charged with carbon dioxide (Sestini, 1891; 6) and according to Toczynski (1871; 2) in hydrocyanic acid.

Van Bemmelen (1882; 2) distinguishes two forms of the hydroxide, first alpha, precipitated from potassium beryllonates by boiling which form is easily washed and, he claims, is the only one of definite composition being readily dried to the formula  $\text{Be}(\text{OH})_2$ , and second beta, which is the gelatinous mass precipitated by alkalies which is always more or less hydrated. Atterberg (1873; 7) gives formulas for some of these hydrated oxides, but there is little in his work or that of Van Bemmelen (1882; 2) to show that this extra water is other than mechanically held. Reubenbauer (1902; 5) found that sodium hydroxide dissolves beryllium hydroxide in proportion to its concentration. Van Bemmelen (1898; 19) studied the effects of heat on his two forms of the hydroxide. Meyer (1899; 3) determined the magnetic susceptibility of the hydroxide. It is readily, although slowly, decomposed by boiling with solutions of ammonium salts (Rose, 1848; 3), Debray (1855; 1), Joy (1863; 1), Parsons (1904; 5, et al.). v. Kobell (1832; 1) states that calcium carbonate will not precipitate beryllium hydroxide in the cold, but does so on boiling. Prudhummer (1805; 7) states that beryllium hydroxide does not act as a mordant.

The *heat of neutralization* of beryllium hydroxide as found by Thomsen (1871; 1, 1874; 2) is

NORMAL COMPOUNDS OF BERYLLIUM



Pettersson (1890; 8) found

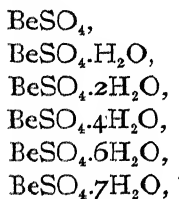


Gmelin (1840; 1), Schaffgotsch (1840; 2), Weeren (1854; 1) and Debray (1855; 1) have also studied the properties of beryllium hydroxide.

**Beryllium Chlorate, Bromate, Iodate,** and compounds of beryllium with oxygen and a halide.

Traube (1894; 3) gives the molecular solution volume of  $\text{Be}(\text{ClO}_3)_2$ , but no details as to the salt itself. Atterberg (1873; 7) prepared the perchlorate,  $\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ , and a periodate to which he gave a very improbable formula. He could not make the chlorate. Marignac (1873; 2) tried to make the bromate and iodate as well, but obtained only indefinite gummy masses. He states further that the perchlorate only takes the crystalline form after concentration to a thick syrup and is very deliquescent. Marignac was probably the nearest correct and it is doubtful if any of these compounds have been made as distinct individuals.

**Beryllium Sulphates.**—Six normal sulphates of beryllium find place in chemical literature:



of which the heptahydrate certainly has no existence, in fact.

**Anhydrous Beryllium Sulphate,  $\text{BeSO}_4$ .**—Nilson and Pettersson (1880; 9) prepared a product very close to the composition  $\text{BeSO}_4$  by heating the dihydrate at  $250^\circ$ . The sulphate so prepared had a specific gravity = 2.443 and a specific heat = 0.1978. Lebeau (1896; 6, 1899; 11) prepared the anhydrous sulphate by the action of strong sulphuric acid on the oxide and evaporation of the excess of acid. Parsons (1904; 10) states that while

420

546.391

1109



the product obtained by either of the foregoing methods is undoubtedly the anhydrous sulphate, it is a very difficult matter to get it pure, owing to the fact that the loss of the last trace of water on heating is very close to the point where sulphur trioxide begins to be given off if indeed the two do not go together. Levi-Malvano (1905; 7) claims that this is a mistake and that he completely eliminated all water at  $218^{\circ}$  to  $220^{\circ}$ .

The anhydrous sulphate is stable in dry air, is itself insoluble in water, but slowly hydrates and goes into solution as the tetrahydrate. It loses sulphuric anhydride even below a red heat, but the last traces are only driven off at a full white heat.

**Beryllium Sulphate Monohydrate**,  $\text{BeSO}_4 \cdot \text{H}_2\text{O}$ .—Levi-Malvano (1905; 7) claims the dihydrate melts at  $158^{\circ}$  and goes over into the monohydrate.

**Beryllium Sulphate Dihydrate**,  $\text{BeSO}_4 \cdot 2\text{H}_2\text{O}$ , is prepared by drying the tetrahydrate at  $100^{\circ}$  and is stable in dry air below this temperature. Nilson and Pettersson (1880; 6), Krüss and Moraht (1890; 7), Parsons (1904; 5, 1904; 10), Levi-Malvano (1905; 7). It dissolves readily in water passing back into the tetrahydrate.

**Beryllium Sulphate Tetrahydrate**,  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ .—The tetrahydrate was first prepared by Berzelius, (1815; 1) who considered it to be an acid salt. Awdejew (1842; 2) first determined its true character and used the salt to determine the atomic weight of beryllium. It was also employed for this purpose by Weeren (1854; 1), Klatzo (1869; 1), Nilson and Pettersson (1880; 6) and Krüss and Moraht (1890; 7). Parsons (1904; 5) showed that the sulphate lost water continuously over phosphoric anhydride and discarded it as a means of determining the atomic weight of the element. This salt of beryllium has been studied more than any other compound of the metal.

**Preparation.**—It is best prepared by dissolving beryllium oxide, carbonate or hydroxide in *excess* of sulphuric acid, evaporating in platinum and heating below a red heat until the larger part, but not all, of the white fumes of sulphuric acid have been driven off, dissolving in water, evaporating to a syrup and turning into strong 95 per cent. alcohol. By this procedure a

milky solution is produced which does not immediately crystallize, but after a few hours the sulphate will have almost entirely separated. To insure perfect freedom from acid two more crystallizations from alcohol are necessary and the salt should finally be crystallized from water to insure the right degree of hydration. The salt may also be prepared more directly and in a fair state of purity by evaporating the sulphuric acid solution to dryness and heating on a sand bath until white fumes cease to come off, taking especial care not to use too high a temperature. The anhydrous sulphate may then be allowed to stand for some time, with occasional stirring, in contact with cold water filtered and the solution evaporated to crystallization.

**Properties.**—Beryllium sulphate tetrahydrate consists of colorless octahedral crystals belonging to the tetragonal system. According to Topsøe (1872; 1) and Topsøe and Christiansen (1873; 9) the crystals are uniaxial and optically negative. Observed forms (011).(110);  $a:c=1:0.9461$ . Mean indices of refraction

C = 1.4374	C = 1.4691
ε D = 1.4395	ω D = 1.4720
F = 1.4450	F = 1.4779

Wulff (1889; 4) states further that the crystals give strong double refraction. Gladstone and Hibbert (1897; 6) compared the molecular refraction of the solid sulphate, 47.41 with the same in solution, 47.94. Jahn (1891; 5) found the specific rotation for the sulphate as 0.28895. The solution friction was studied by Wagner (1890; 12). Meyer (1899; 3) studied the magnetic susceptibility. Traube (1894; 3) determined the molecular solution volume. Höber (1898; 9) found that the sulphate and chloride have same sweet taste at equal cation concentrations. According to Leys (1899; 10) and Brunner (1900; 1) the sulphate is less hydrolyzed in solution than the sulphates of aluminum and iron. Brunner gives this hydrolysis in N/4 to N/20 solution as 0.52 per cent. to 0.68 per cent. According to Weeren (1854; 1) the crystals lose one-third of their water of crystallization at 35°. Parsons (1904; 5) by tensimeter experiments found the vapor tension of the crystals at 20° to equal a pressure of 20 millimeters of olive oil and to increase rapidly

with the temperature. Over phosphoric acid the crystals lose water slowly at ordinary temperatures. By dissolving one mol  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  in 400 mols of water Thomsen (1873; 4) found the heat of solution  $= +1100$ . Pollok (1904; 9) gives the heat of solution as  $0.85\text{K}^\circ$ . The specific gravity has been determined as follows: Topsøe (1872; 1) (1873; 6) 1.725; Nilson and Pettersson (1880; 9) 1.713; Stallo (Clark's "Constants of Nature") 1.6743 at  $22^\circ$ ; Krüss and Moraht (1890; 7) 1.7125.

Beryllium sulphate tetrahydrate is soluble in about its own weight of water, but is insoluble in absolute alcohol. Its solution is strongly acid to indicators, attacks zinc with evolution of hydrogen and when fully concentrated dissolves two equivalents of its own hydroxide. On dilution the main portion of the hydroxide is thrown down, but approximately one-half of an equivalent remains dissolved at infinite dilution. It should be crystallized from a neutral or acid solution, for although the crystals can be obtained from a basic solution (1906; 5) it is impossible to separate them therefrom. The taste of the salt is a mixed acid and sweet.

**Beryllium Sulphate Hexahydrate.**—Marignac (1873; 1), in attempting to repeat Klatzo's work (1869; 1) on the heptahydrate, after many attempts obtained *only once*, by evaporating a supersaturated solution of sodium sulphate and beryllium sulphate, a mass of prismatic crystals which he thought contained six molecules of water. They immediately effloresced on exposure to air and could not have been the hexahydrate described by Levi-Malvano (1905; 7). According to the last named author he obtained crystals of the hexahydrate from a commercial source and after repeated trials was able to produce the salt itself by treating an excess of but a little diluted sulphuric acid with enough beryllium hydroxide or carbonate at ordinary temperatures to insure a state of *supersaturation* of the sulphate formed and suddenly shaking the mass. The solution itself should contain excess of acid, and inoculation with crystals of the hexahydrate previously produced was apparently of no assistance. Crystallization in the cold did not seem to especially favor the formation of the hexahydrate, but the one condition

seemed to be supersaturation. Still having once produced the hexahydrate it could be crystallized out of aqueous solution at temperatures as high as  $50^{\circ}$  and he even threw it out of solution at  $90^{\circ}$  by addition of boiling alcohol. On the other hand when at  $-30^{\circ}$  the cryohydrate was reached, the hexahydrate was present mixed with ice. According to Levi-Malvano the hexahydrate is stable in air. The finely pulverized salt melted at  $78.8^{\circ}$ , but on removing the source of heat and cooling, the solidification point of the syrupy liquid was found to be  $68.4^{\circ}$ . This was probably due to a mixture of crystals of a lower hydrate. The solubility curve of the hexahydrate which is given cuts that of the dihydrate at  $77.4^{\circ}$ . The hexahydrate on ignition loses water and yields a *blue* oxide.

Parsons and Fuller (1906; 5) made many attempts to produce the hexahydrate, but without success and think that some condition besides supersaturation must be essential. An order sent to the dealers from whom Levi-Malvano first obtained his salt brought a bottle labeled "hexahydrate," but which on examination proved to be nothing but the regular tetrahydrate.

**Beryllium Sulphate Heptahydrate.**—Klatzo (1869; 1) thought he had produced a hydrate with seven molecules of water of crystallization. His work is unconfirmed and the conditions which he gives, would in themselves, seem to render its production improbable, if not impossible. Parsons (1904; 10) states that this hydrate undoubtedly does not exist. It should be remembered also that Marignac (1873; 1) found Klatzo's work to be incorrect in many particulars.

**Beryllium Sulphite,  $\text{BeSO}_3$ .**—The normal salt has been produced only by Krüss and Moraht (1890; 5) who prepared it by adding freshly precipitated beryllium hydroxide which had been dried by washing with alcohol, to alcohol saturated with sulphur dioxide and evaporating over phosphoric anhydride. It consists of colorless hexagonal plates which are immediately decomposed by water yielding sulphur dioxide and beryllium hydroxide. For several so-called basic compounds see basic salts. Atterberg (1873; 7) could not produce a sulphite.

**Beryllium Thiosulphite.**—Factor (1901; 5) claims to have produced the salt,  $\text{BeS}_2\text{O}_3 \cdot 11\text{H}_2\text{O}$ , by the action of a solution of sodium thiosulphate on a solution of beryllium sulphate. Some experiments by the author lead him to believe that this is incorrect for in his hands an admixture of these two solutions always precipitates sulphur and gives off sulphur dioxide as was to be expected. Marignac (1875; 1) and Atterberg (1873; 7) could not obtain the salt.

**Beryllium Dithionate.**—The normal salt has not been produced.

**Beryllium Sulphocyanate,**  $\text{Be}(\text{CyS})_2$ .—Hermes (1866; 2) concluded that the somewhat illy defined residue obtained by the action of the acid on beryllium carbonate was the sulphocyanate. Found it to be soluble in alcohol. Toczynski (1871; 2) was unable to prepare the sulphocyanate with any definiteness and Atterberg (1873; 7) had no better success.

**Beryllium Selenate,**  $\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$ .—Beryllium selenate was first prepared by Atterberg (1873; 7 and 8) and has been also studied by Topsøe (1872; 1). It is isomorphous with the sulphate and like the sulphate, loses water at  $100^\circ$  forming a dihydrate. According to Topsøe (1872; 1) and Topsøe and Christiansen (1873; 9), it crystallizes in the rhombohedral system,  $a:b:c=1:0.9602:0.9027$ , observed forms (011), (101), (021), (111), (001). Its mean indices of refraction are

	$\mu_a$	$\mu_b$	$\mu_c$
C	1.4992	1.4973	1.4639
D	1.5027	1.5017	1.4664
F	1.5101	1.5084	1.4725

Its specific gravity (Topsøe) is 2.029. Roozeboom (1891; 1) and Topsøe (1872; 1) have both discussed the significance of the mixed crystals of the sulphate and selenate.

**Beryllium Selenite,**  $\text{BeSeO}_3 + \text{Aq}$ .—Two normal selenites find place in literature,  $\text{BeSeO}_3 \cdot \text{H}_2\text{O}$ , prepared by Atterberg (1873; 7) and  $\text{BeSeO}_3 \cdot 2\text{H}_2\text{O}$ , prepared by Nilson (1875; 2). Nilson states that his salt loses one molecule of water at  $100^\circ$ . It was a gummy mass decomposable by water and made by evaporating the constituents together. Formula arrived at by analysis of gummy mass and no evidence of individual ex-

istence. Acid selenites (see acid salts) and so-called basic selenites (see basic salts) have been prepared in much the same way. None of these salts should be accepted without confirmation.

**Beryllium Tellurates and Tellurites.**—Berzelius (1833; 2) precipitated beryllium tellurate and tellurite from solution by means of the corresponding potassium salt. They were obtained as white voluminous flakes, and were probably basic mixtures but no details are given.

**Beryllium Chromite,**  $\text{BeCr}_2\text{O}_4$ .—A crystalline compound made by Ebelmen by fusing chromic oxide, beryllium oxide and boric anhydride together and treating with hydrochloric acid. Described by Mallard (1887; 4).

**Beryllium Chromate.**—Atterberg (1873; 7) attempted to produce a neutral chromate but was not successful. The author of this summary and his students have repeatedly attempted to produce a chromate of definite composition, by crystallizing from aqueous solutions of very varied acid concentration treated with basic carbonate, to all degrees of saturation, and evaporated both in vacuo and in the air, but without success. If chromic acid was present in excess it crystallized out first and no separation of another definite compound could be obtained, although it was of course a simple matter to obtain residues containing any desired ratio between the beryllium and chromic acid. If carbonate was added to saturation or even in excess of the equivalent amount and long before the solution was neutralized only the usual indefinite gummy basic chromates were obtained on evaporation. On the other hand Glassmann (1907; 4) claims to have made a neutral chromate,  $\text{BeCrO}_4 \cdot \text{H}_2\text{O}$ , by "neutralizing" a chromic acid solution with basic carbonate and evaporating, which he states are reddish yellow monoclinic crystals, decomposed by water.

**Beryllium Molybdate,**  $\text{BeMoO}_3 \cdot 2\text{H}_2\text{O}$ .—prepared by Rosenheim and Woge (1897; 4) by boiling equivalents of molybdic acid and beryllium hydroxide suspended in water. An oily liquid layer so obtained was separated in a separatory funnel and after standing two weeks in the cold of winter solidified to an aggre-

gate of needle like crystals. Analysis shows decided basicity which they attribute to admixture of beryllium hydroxide impossible to remove.

**Beryllium Nitrate.**—The normal nitrate was an article of commerce before it found place in literature. Ordway (1858; 1, 1859; 2) made a special study of the nitrates and found, as had been the case with Vauquelin (1798; 5) and Gmelin (1801; 1) that they are extremely difficult to crystallize. By precipitating a solution of beryllium sulphate with barium nitrate and evaporating the solution over sulphuric acid, Ordway produced a solid mass that approached the normal nitrate in composition, but still basic as would necessarily result from any method involving the presence of water in quantity. Ordway shows how readily the nitrate loses nitric anhydride and Parsons (1904; 5) has shown that by evaporating a solution of the nitrate it becomes strongly basic below  $50^{\circ}$ , and on slowly drying to  $175^{\circ}$  it has become a solid which has already lost 75 per cent. of its nitric anhydride. Atterberg (1873; 7) could make no nitrate.

The commercial crystallized nitrate, which can be obtained almost perfectly pure, as it is used in the incandescent mantle industry, smells strongly of nitric anhydride, melts with very little heat in its own water of crystallization and immediately begins to show bubbles of escaping gas. On slowly increasing the heat, the nitric anhydride is rapidly evolved leaving behind a viscous glucose like mass, which is still readily soluble in water when it has reached the tribasic condition. Even below  $175^{\circ}$  it has become tetrabasic and loses all of its nitric anhydride below a red heat. The resultant oxide contains a small amount of occluded oxygen and nitrogen, which if the decomposition has been gradually brought about, is equivalent to approximately 0.35 cubic centimeter (Parsons, 1904; 5) of mixed gases, of which approximately two-thirds are nitrogen, per gram of oxide. The nitrate is, of course, strongly acid in reaction. According to Brunner (1900; 1), a solution of the nitrate of normality N/10 to N/40 is hydrolyzed from 1.8 per cent. to 1.9 per cent.

The nitrate is easily made (1906; 13) by saturating nitric acid with basic beryllium carbonate, evaporating to a syrupy con-

sistency, adding strong nitric acid in excess and crystallizing therefrom. The crystals obtained are definite in composition and have the composition,  $\text{Be}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ . They are highly deliquescent, lose nitric acid readily, and are stable only in presence of strong nitric acid or in equilibrium with its vapor. They melt in their own water of crystallization at 60.5 and are soluble in alcohol and acetone.

**Beryllium Nitrite.**—Beryllium nitrite has never been prepared. The efforts of Vogel (1903; 2) proving fruitless as the solution immediately hydrolyzed with loss of the oxides of nitrogen. It may possibly be prepared in non-aqueous solutions.

**Beryllium Phosphate.**—The literature of the normal phosphates of beryllium is very far from clear, as the few investigators who have taken up the matter have found the material they produced of a gelatinous nature and difficult to identify as an individual salt. Sestini (1890; 2), by boiling an acetic acid solution of beryllium phosphate, obtained a flocculent precipitate to which he gave the formula,  $\text{Be}_3(\text{PO}_4)_2 \cdot 3\text{H}_2\text{O} + \text{Aq.}$  Atterberg (1873; 7) obtained, by adding sodium orthophosphate to a soluble beryllium salt, a flocculent precipitate to which he assigned the formula,  $\text{Be}_3(\text{PO}_4)_2 \cdot 6\text{H}_2\text{O}$ . Prepared by precipitating a phosphoric acid solution of beryllium hydroxide with alcohol it contained  $7\text{H}_2\text{O}$ .

**Beryllium Hypophosphate.**  $2\text{BePO}_3 + 3\text{H}_2\text{O}$ .—Rammelsberg (1891; 4) in his studies of the hypophosphates threw down a hot solution of beryllium sulphate with sodium hypophosphate and obtained a white precipitate having the composition,  $2\text{BePO}_3 + 3\text{H}_2\text{O}$ , which on heating to  $230^\circ$ - $250^\circ$  lost one-half of its water.

**Beryllium Pyrophosphate.**  $\text{Be}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ .—By precipitating a solution of sodium pyrophosphate with a basic solution of beryllium nitrate, Scheffer (1859; 3) obtained a white pulverulent precipitate which, on analysis, yielded results close to the theoretical formula for the pyrophosphate. Atterberg (1873; 7) studied the reaction, but did not identify the salt.

**Beryllium Phosphite and Hypophosphite.**—Rose (1827; 1) pre-



precipitated a solution of beryllium chloride with a solution of phosphorus trichloride in ammonia and again (1828; 1) saturated hypophosphorous acid with beryllium hydroxide, obtaining a gummy mass. Probably neither precipitate was the normal salt and no formula was assigned.

**Beryllium Vanadate.**—Berzelius (1831; 3) in his researches on the vanadates obtained a yellow, neutral, difficultly soluble beryllium vanadate which was not studied and to which no formula was assigned.

**Beryllium Arsenate,**  $\text{Be}_3(\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ .—Prepared by Atterberg (1875; 4). Made in the same way as the corresponding phosphate which it resembled. Almost no other details.

**Beryllium Antimonate,**  $\text{Be}(\text{SbO}_3)_2 \cdot 6\text{H}_2\text{O}$ .—This salt was prepared by Ebel (1887; 2) by adding a soluble beryllium salt to a hot solution of sodium metantimonate.

**Beryllium Columbate.**—By precipitating beryllium chloride with potassium columbate and fusing the precipitate in boric anhydride Larsson (1896; 10) succeeded in obtaining a crystalline columbate containing 6.24 per cent.  $\text{BeO}$  and 89.60 per cent.  $\text{Cb}_2\text{O}_5$ .

**Beryllium Carbonate.**—No normal carbonate of beryllium is known. The carbonate,  $\text{BeCO}_3 \cdot 4\text{H}_2\text{O}$ , claimed by Klatzo (1869; 1), was a mistake and has never been made, and can not be made unless from non-aqueous solution. The so-called basic carbonates are important and several double carbonates are known (see basic salts and double carbonates).

**Beryllium Silicates.**—The work on the normal silicates of beryllium has been confined to the artificial production of a meta silicate,  $\text{BeSiO}_3$ , phenacite,  $\text{Be}_2\text{SiO}_4$ , and beryl,  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ . Phenacite was first prepared by Ebelmen (1887; 4) by fusing together silicon dioxide, beryllium oxide and borax in right proportions. Later Hautefeuille and Perrey (1888; 4) prepared it by fusing  $\text{SiO}_2$  and  $\text{BeO}$  together using lithium vanadate and carbonate as a mineralizing agent, and still later (1890; 14, and 1893; 1) by fusing beryllium sulphate and silicic acid. Beryl was first prepared by Williams (1873; 3), by directly fusing together its constituents and later, Hautefeuille and Perrey (1888; 4) prepared it by fusing together its constituents in acid lithium

molybdate. Stein (1907; 9) by fusing in a carbon tube the necessary quantities of  $\text{BeO}$  and  $\text{SiO}_2$  at  $2000^\circ$  obtained a meta silicate,  $\text{BeSiO}_3$  with density 2.35 and an ortho silicate with density 2.46.

**Beryllium Silicotungstate.**—Wyrouboff (1896; 1) prepared a crystalline silicotungstate to which he gave the incomprehensible formula,  $\text{Be}_4(\text{W}_{12}\text{SiO}_{40})_3 \cdot 93\text{H}_2\text{O}$ , when crystallized below  $45^\circ$ . Crystallized above  $45^\circ$  it becomes rhombohedral with  $87\text{H}_2\text{O}$ . In presence of nitric acid at  $30^\circ$  a  $45\text{H}_2\text{O}$  compound is obtained.

**Beryllium Fluosilicate.**—Berzelius (1823; 1) prepared a fluosilicate by the action of fluosilicic acid on beryllium hydroxide, but did not analyze or give details, and both Atterberg (1873; 7) and Marignac (1873; 1) state that it can be made only in solution.

**Beryllium Aluminate,  $\text{Be}(\text{AlO}_2)_2$ .**—Occurs in nature as chrysoberyl (cymophane, alexandrite) and prepared artificially by Ebelmen (1851; 3) by fusing theoretical portions of alumina and beryllia in boric anhydrid and later, by Hautefeuille and Perrey by fusing a mixture of the oxides of aluminum and beryllium in leucite or nephelite.

**Beryllium Ferrocyanide and Ferricyanide.**—Toczynski (1871; 2) prepared beryllium ferrocyanide by adding beryllium sulphate to barium ferrocyanide as a light green mass. By oxidizing with chlorine, he obtained the ferricyanide as an olive green material. Both were poorly defined and probably basic in nature as Atterberg (1873; 7) has pointed out.

**Beryllium Nitroprusside.**—Toczynski (1871; 2) was not able to prepare a nitroprusside.

**Beryllium Methyl,  $\text{Be}(\text{CH}_3)_2$ ; Beryllium Ethyl,  $\text{Be}(\text{C}_2\text{H}_5)_2$ ; Beryllium Propyl,  $\text{Be}(\text{C}_3\text{H}_7)_2$ .**—Beryllium ethyl was first prepared by Cahours (1860; 1) by the action of metallic beryllium on ethyl iodide in a sealed tube. In later experiments, (1873; 1), he produced enough to study by the action of beryllium on mercury ethyl. Found it to be a colorless liquid boiling at  $185^\circ$ – $188^\circ$ . It is spontaneously combustible in air and is decomposed by water. It can be distilled in an atmosphere of carbon dioxide. *Beryllium propyl* was also prepared by Cahours (1873; 1)

in a similar manner by the action of beryllium on mercury propyl in a sealed tube at  $130^{\circ}$ - $135^{\circ}$ . It was also a liquid boiling at  $244^{\circ}$ - $246^{\circ}$  with properties similar to beryllium ethyl.

*Beryllium methyl* was later prepared by Lavroff (1884; 3) in a similar manner by the action of metallic beryllium on mercury methyl in a sealed tube at  $130^{\circ}$ . It is a white volatile crystalline substance decomposed by water with evolution of light, into methane and beryllium hydroxide.

**Beryllium Formate, Acetate, Propionate, Etc.**—Although many attempts were made by Vauquelin (1798; 5), Urbain and Lacombe (1901; 2, 1902; 3) and others, *normal* salt of beryllium with any member of the fatty acids was made until Steinmetz (1907; 5) finally succeeded in preparing the normal acetate,  $\text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2$ , by heating equal parts of basic acetate,  $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ , and glacial acetic acid with five to six parts of acetic anhydride for two hours in a sealed tube at  $140^{\circ}$ . He obtained under these conditions crystals of the normal acetate, as small double refracting leaflets, which were insoluble in water, alcohol, ether, and other organic solvents. They melted with decomposition at  $300^{\circ}$  yielding a sublimate of the basic acetate. They were also slowly hydrolyzed by boiling water.

Tanatar (1907; 12) claims to make the normal formate,  $\text{Be}(\text{CHO}_2)_2$ , by slowly evaporating over sulphuric acid a solution of formic acid neutralized with the basic carbonate. He also claims to make the basic formate,  $\text{Be}_4\text{O}(\text{CHO}_2)_6$ , by mixing the calculated weights and boiling in water. While it is a simple matter to get a mass under these conditions that will give almost any desired per cent. of  $\text{BeO}$ , which was his apparent criterion, anyone familiar with the real properties of the element would know that neither of these salts could possibly be made under these conditions. Tanatar apparently did, however, make the normal propionate,  $\text{Be}(\text{C}_3\text{H}_5\text{O}_2)_2$ , by heating, at  $150^{\circ}$ , the basic propionate with propionic acid mixed with its anhydrid. It is little affected by solvents as Steinmetz (1907; 5) found to be the case with the acetate.

**Beryllium Acetylacetonate**,  $\text{Be}(\text{C}_6\text{H}_7\text{O}_2)_2$ .—Beryllium acetylacetonate is one of the most interesting of the salts of beryllium. It was first prepared by Combes (1894; 6) by the action of

acetylacetone on a solution in equivalent quantities of beryllium hydroxide in acetic acid. He found it to be a white crystalline solid melting at  $108^{\circ}$ , easily sublimed, and boiling at  $270^{\circ}$ . Two determinations of its vapor density showed its molecular weight to correspond with the formula,  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ . Parsons (1904; 5) who used this salt as a basis in his atomic weight determinations made a careful study of the compound. He found it to be most readily prepared by the direct action of acetylacetone on basic beryllium carbonate or hydroxide. According to this author, the specific gravity of beryllium acetylacetonate is 1.168 compared to water at  $4^{\circ}$ . It is a perfectly white crystalline substance which is slightly soluble in cold water, more soluble in hot water and slowly hydrolyzed by boiling water with loss of acetylacetone and precipitation of beryllium hydroxide. It is readily soluble in alcohol and is easily crystallized therefrom in rhombic plates. It is soluble in benzene, toluene, xylene, naphtha, and all petroleum distillates, chloroform; turpentine, methyl alcohol, amyl alcohol, ether, ethyl acetate, acetone and carbon disulphide. It sublimes many degrees below its boiling point and begins to sublime even below the boiling point of water. The sublimed crystals are light and flocculent with a marked resemblance to flakes of snow. It is soluble in acids setting free acetylacetone.

**Beryllium Oxalate Trihydrate**,  $\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$ .—Although early attempts were made by Vauquelin (1798; 5), Debray (1855; 1) and Atterberg (1873; 7) to produce the normal oxalate, they were not successful and it was first made by Rosenheim and Woge (1897; 4). Wyruboff (1902; 1) confirms the results of Rosenheim and Woge, and Parsons and Robinson (1906; 1) made a study of the system,  $\text{BeO}:\text{C}_2\text{O}_3:\text{H}_2\text{O}$ , also producing the normal oxalate. All three authors produced their oxalate by adding basic beryllium carbonate or hydroxide to excess of oxalic acid and crystallizing the oxalate therefrom. It was found almost impossible to get the salt absolutely free from excess of oxalic acid by crystallization and to procure the perfectly neutral salt. Parsons and Robinson added the necessary measured quantity of beryllium basic carbonate. Any excess of base pre-

vented crystallization. The crystals of the trihydrate were described by Wyruboff (1902; 1). The crystals were figured in the article of Parsons and Robinson and the measurements made by Penfield and Heath (1906; 1) showed the crystals to be orthorhombic. The forms observed  $c(001)$ ,  $d(101)$ ,  $p(111)$ . The angles

$$P \wedge P'', 111 \wedge \bar{1}\bar{1}\bar{1} = 74^{\circ}16'$$

$$P \wedge P, 111 \wedge \bar{1}\bar{1}\bar{1} = 90^{\circ}6'$$

$$C \wedge P, 001 \wedge 111 = 68^{\circ}30'$$

$$\text{Calculated } 68^{\circ}20'$$

The first two measurements yielded the axial ratio  $a:b:c=0.853:1.0:1.645$ . No distinct cleavage was observed. The  $c$  axis is a bisectrix and the plane of the optical axis is the brachypinacoid. In the crystal examined, the interference figure was indistinct and the axial angle so large that the hyperbolas opened out beyond the field of view.

Beryllium oxalate trihydrate is stable at room temperature. It is soluble in less than its own weight of boiling water and is but little less soluble at ordinary temperatures. It is strongly acid in reaction and in concentrated solution dissolves 1.85 equivalents of its own carbonate or hydroxide. It has a sharp sweetish taste. Heated at  $100-105^{\circ}$  it loses two thirds of its water of crystallization forming the monohydrate.

**Beryllium Oxalate Monohydrate.**—Prepared by Rosenheim and Woge (1897; 4), Wyruboff (1902; 1) and by Parsons and Robinson (1906; 1). Is made by heating the trihydrate at  $100-105^{\circ}$ . Heated much above this temperature it begins to lose water, at first slowly, but more rapidly as the thermometer reaches  $220^{\circ}$ , at which temperature the oxalate begins to decompose and at  $350^{\circ}$  is completely converted into the oxide.

**Beryllium Tartrate**,  $\text{BeC}_4\text{H}_4\text{O}_6 + 3\text{H}_2\text{O}$ .—Vauquelin (1898; 5) and Toczynski (1871; 1) attempted the production of the normal tartrate, but it was first reported by Atterberg who gave to it the formula,  $\text{BeC}_4\text{H}_4\text{O}_6 + 3\text{H}_2\text{O}$ . Atterberg gives few details, but the salt is confirmed by Rosenheim and Itzig (1899; 15) who simply state the fact. The chief characteristic of the tartrates of beryllium and a fact which gives them especial interest is

their abnormally great rotatory power. This fact was first brought out by Biot (1838; 1) on a tartrate of unstated composition prepared by Berthier, who found the beryllium tartrate to have the largest specific rotatory power of any tartrate examined, viz., in 100 millimeters  $+41.134$  to  $+43.992$ . Rosenheim and Itzig (1899; 13) in their work on some double tartrates, (which see) confirm this fact and found the rotation of polarized light, both right and left, was greatly increased by the incorporation of beryllium in the molecule. By saturating tartaric acid with freshly precipitated beryllium hydroxide at boiling heat and evaporation, they obtained a basic uncrystallizable glassy mass whose analysis led to the formula,  $\text{Be}_3\text{C}_4\text{H}_2\text{O}_7 \cdot 7\text{H}_2\text{O}$ , which had a very high rotatory power, their four experiments giving  $[\text{M}]_D = +171^\circ$  to  $+176.8^\circ$ . The rotatory power showed a change on dilution owing to hydrolysis and the authors were inclined to believe they had here a beryllium salt of diberyllium tartrate, similar to potassium diberyllium tartrate, to be described later.

**Beryllium Succinate**,  $\text{BeC}_4\text{H}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$ .—Atterberg (1893; 7) obtained this salt by dissolving the hydrate or carbonate in excess of succinic acid and concentrating at a thick syrup from which small crystals separated. These crystals lost their water of crystallization at  $100^\circ$ . They are only stable in presence of an excess of succinic acid.

**Beryllium Picrate**.—Lea (1858; 2) reports a golden yellow crystalline picrate made by dissolving basic beryllium carbonate in picric acid. No analysis, and it was probably basic. Glassmann, (1907; 6) by "neutralizing" picric acid solution with basic beryllium carbonate obtained yellow scales which he dried in the air and assigned the formula,  $\text{Be}(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2 \cdot 3\text{H}_2\text{O}$ . By washing with ether, he dried it somewhat and assigned  $\text{Be}(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2 \cdot 2\text{H}_2\text{O}$  to the product, and since by drying at  $120^\circ$ - $130^\circ$  he obtained a product which gave a molecular lowering in acetophenone corresponding to 465 and a BeO content nearly theoretical, he assumed he had anhydrous  $\text{Be}(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2$ . He apparently measured his lowering only to the second decimal and a slight error would have given a very different result,

especially as it has been shown (1907; 10) that dissolving beryllium hydroxide in solutions of its normal salts raises the freezing point. If he obtained a "neutral" solution these are the only conditions that could have prevailed. As he, himself, claims that water (in which it was made) decomposes the picrate and as oxide content is no criterion of composition, especially with beryllium salts, his results need confirmation before being accepted.

**Beryllium Alpha Brom Camphor Sulphonate.**  $\text{Be}(\text{C}_{10}\text{H}_{14}\text{BrO}_2\text{SO}_2)_2$ , was prepared by Walden (1894; 7) and although he gives no detail of the salt itself, he studied its optical rotation in comparison with the analogous magnesium, zinc and barium salt in dilute solution and found for same molecular concentration essentially the same rotation. Concluded that the beryllium ions were therefore inactive. Biot (1838; 1) and Rosenheim and Itzig (1899; 13) would seem to be led to a contrary conclusion in the case of the tartrate unless, as indeed Rosenheim and Itzig indicate, a complex ion is formed.

**Beryllium Rhodizonate,**  $\text{Be}(\text{H}_2\text{C}_4\text{O}_6)$ ; **Beryllium Kroconate,**  $\text{Be}(\text{HC}_5\text{O}_4)$ .—Two substances reported by Heller (1837; 1). The first was a brown powder and the second yellow crystals. Both made by treating an alcoholic solution of the corresponding acid with beryllium acetate.

**Beryllium Citraconate,**  $\text{BeC}_7\text{H}_4\text{O}_6$ ; **Beryllium Fumarate,** **Beryllium Maleate,**  $\text{BeC}_4\text{H}_2\text{O}_4$ . Have no basis for a claim to existence except the BeO content of a substance made by Tanatar (1907; 12), by treating the corresponding acid with basic carbonate and evaporating. There is nothing to indicate that they are not the usual indefinite basic mixtures obtained under these conditions.

## CHAPTER IV

### ACID SALTS OF BERYLLIUM.

Beryllium has very little tendency to form acid salts and only an acid oxalate, an acid molybdate, an acid phosphate, an acid arsenate and four acid selenites have place in chemical literature. The first has been shown to be a simple mixture of the normal oxalate and oxalic acid, and the molybdate and selenites were little more than the residues left on evaporating the constituents with little of detail in their study. The phosphate was non-crystalline. These salts need confirmation although from the well known tendencies of phosphoric acid, the existence of an acid phosphate would seem as probable as any acid salt of beryllium.

**Beryllium Monoacid Phosphate,  $\text{BeHPO}_4 \cdot 3\text{H}_2\text{O}$ .**—Sheffer (1859; 3) precipitated a nitric acid solution of beryllium with disodium acid phosphate, obtaining a white non-crystalline powder, and gave the formula,  $\text{BeHPO}_4 \cdot 3\text{H}_2\text{O}$ , to the precipitate formed. He found it lost two molecules of water on drying. Atterberg (1875; 4) also obtained the same substance by solution of the hydroxide in phosphoric acid and precipitating with alcohol. A viscous mass was obtained which analyzed near to the above formula. By dissolving in phosphoric acid and precipitating with alcohol, Sheffer thought the mass formed had the composition,  $5\text{BeO} \cdot 2\text{P}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$ .

**Beryllium Acid Arsenate,  $\text{BeHASO}_4 \cdot 2\text{H}_2\text{O}$ .**—Reported by Atterberg (1875; 4) as resembling the corresponding phosphate and made in the same way.

**Beryllium Acid Selenites.**—Nilson (1875; 2 and 1875; 3) reported four beryllium selenites apparently acid in nature,  $\text{BeSeO}_3 \cdot \text{H}_2\text{SeO}_3$ ,  $\text{BeSeO}_3 \cdot 2\text{H}_2\text{SeO}_3$ ,  $5\text{BeO} \cdot 8\text{SeO}_2 \cdot 5\text{H}_2\text{O}$  and  $3\text{BeO} \cdot 7\text{SeO}_2 \cdot 5\text{H}_2\text{O}$ . Whether these substances are mixtures or definite individuals needs confirmation, as they were little more than the residues left on evaporating the constituents together.



Atterberg (1873; 7) did not succeed in making any acid selenites, although he obtained the usual basic mixture.

**Beryllium Acid Oxalate.**—Rosenheim and Woge (1897; 4) reported the compound,  $2\text{BeC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$ . This was investigated by Parsons and Robinson (1906; 1) who showed that the substance is simply a mixture of the normal oxalate and oxalic acid. All attempts to make it as a distinct substance met with failure.

**Beryllium Acid Molybdate.**—Atterberg (1873; 7) reported an acid molybdate,  $\text{BeMoO}_4 + \text{MoO}_3 + \text{vAq.}$  but gives little detail.

## CHAPTER V

### DOUBLE SALTS OF BERYLLIUM.<sup>1</sup>

Many well defined and crystalline double salts of beryllium have been made. In many cases the double salts are readily prepared and are quite stable when the normal single salt can not be produced at all or only in the absence of water. This is notably true in the case of the double carbonates, chlorides, iodides, nitrites and sulphites. In general these salts have been but little studied, their discoverers being content with their identification and analysis. Being less subject to the confusing action of hydrolysis than either the normal or basic salts of beryllium, their description and identity can, as a rule, be depended upon when found in literature.

#### DOUBLE CHLORIDES.

**Potassium Beryllium Chloride**,  $\text{BeCl}_2 \cdot 2\text{KCl}$ .—Enumerated by H. L. Wells (1901; 3) in his list of double halides. Authority has not been found. Welkow (1874; 6) could not obtain a double chloride with either potassium or sodium.

**Mercury Beryllium Chloride**,  $2\text{BeCl}_2 \cdot 3\text{HgCl}_2 + 6\text{H}_2\text{O}$ .—A double chloride with mercury has been reported by two observers, first by Bonsdorff (1828; 4) who simply states it was obtained in rhombic prisms, but gives no analysis or formula, and second by Atterberg (1873; 7) who obtained it in large tabular hydroscopic crystals by evaporation of like equivalents of the two chlorides in excess of strong hydrochloric acid. Marignac (1873; 1) could not obtain the double salt and states that it is a mistake and the  $\text{HgCl}_2$  crystallizes out alone.

**Auric Beryllium Chloride**,  $\text{BeCl}_2 \cdot \text{AuCl}_3$  and  $\text{BeCl}_2 \cdot 2\text{AuCl}_3$ .—Obtained by Atterberg (1873; 7) together from a solution of like equivalent, allowed to stand for a long time over sulphuric acid. The first crystallized as tetragonal double pyramids and later the crystals of the second form settled out.

<sup>1</sup> Some salts are included here which are possibly not true double salts but salts of a complex acid.

**Stannic Beryllium Chloride.**  $\text{BeCl}_2 \cdot \text{SnCl}_4 \cdot 8\text{H}_2\text{O}$ . Atterberg (1873; 7), by dissolving tin chloride and beryllium oxide in excess of hydrochloric acid and evaporating over sulphuric acid, obtained some ill defined rhombic pyramids. They deliquesced easily in air. Marignac (1873; 1) was not able to obtain any double salt with tin.

**Ferric Beryllium Chloride.**  $\text{BeCl}_2 \cdot \text{FeCl}_3 \cdot \text{H}_2\text{O}$ . Orange yellow crystals obtained by adding beryllium chloride to warm concentrated hydrochloric acid (1.19 specific gravity) to which a large amount of ferric chloride had already been added and allowing the solution to cool. Neumann (1888; 10).

**Chromic Beryllium Chloride.**  $\text{BeCl}_2 \cdot \text{CrCl}_3 \cdot \text{H}_2\text{O}$ . Prepared as violet hygroscopic crystals by Neumann (1888; 1) by dissolving chromic chloride in strong alcohol, adding some beryllium chloride and passing hydrochloric acid gas through the heated mixture.

**Thallic Beryllium Chloride.**  $3\text{BeCl}_2 \cdot \text{TlCl}_3$ . By dissolving thallium oxide and beryllium chloride in strong hydrochloric acid and oxidizing with chlorine, Neumann (1888, 1) obtained rhombic tabular crystals of the above formula.

**Iodic Beryllium Chloride.**  $\text{BeCl}_2 \cdot 2\text{ICl}_3 \cdot 8\text{H}_2\text{O}$ . Obtained by Weinland and Schlegelmilch by passing a current of chlorine through a cold strong hydrochloric acid solution of beryllium chloride to which an excess of iodine had been added. Gold yellow needles, very unstable and hygroscopic.

**Platinous Beryllium Chloride.**  $\text{BeCl}_2 \cdot \text{PtCl}_2 \cdot 5\text{H}_2\text{O}$ . Nilson (1876; 2) prepared the beryllium chloroplatinate by evaporating together platinum dichloride and beryllium chloride in hydrochloric acid solution. Obtained dark red crystals soluble in water, which at  $100^\circ$  lost both water and hydrochloric acid.

**Platinic Beryllium Chloride.**  $\text{BeCl}_2 \cdot \text{PtCl}_4 \cdot 8\text{H}_2\text{O}$ . First prepared by Thomsen (1870; 1) by dissolving beryllium hydroxide in a hydrochloric acid solution of platinic chloride and crystallizing. Thomsen assigned  $9\text{H}_2\text{O}$ , but was corrected by Marignac (1873; 3). Further by heating at  $120^\circ$ , he found his crystals lost water and then had the composition,  $\text{BeCl}_2 \cdot \text{PtCl}_4 \cdot 4\text{H}_2\text{O}$ . It was later prepared by Welkow (1873; 5). The crystals are

dark yellow or orange, four, six, or eight-sided prisms, soluble in alcohol and very hygroscopic.

**Palladous Beryllium Chloride**,  $\text{BeCl}_2 \cdot \text{PdCl}_2 \cdot 6\text{H}_2\text{O}$ .—Welkow (1874; 6), by heating a concentrated solution of beryllium palladic chloride, caused it to lose chlorine and obtained brown tabular, hygroscopic crystals having the above formula and readily soluble in water and alcohol.

**Palladic Beryllium Chloride**,  $\text{BeCl}_2 \cdot \text{PdCl}_4 \cdot 8\text{H}_2\text{O}$ .—Obtained by Welkow (1874; 3) as small, dark, reddish brown, quadratic tables by evaporating a solution of the constituents over sulphuric acid. It is isomorphous with the corresponding platinum salt, but loses all of its water at  $130^\circ$ .

#### DOUBLE FLUORIDES.

**Potassium Beryllium Fluoride**,  $\text{BeF}_2 \cdot \text{KF}$  and  $\text{BeF}_2 \cdot 2\text{KF}$ .—Two double fluorides of potassium are known. The second of these was produced as early as 1811 by Gay Lussac and Thenard and again in 1823 by Berzelius, but they made no analyses. Awdejew (1842; 2) prepared and studied  $\text{BeF}_2 \cdot 2\text{KF}$  and Debray (1855; 1),  $\text{BeF}_2 \cdot \text{KF}$ . Gibbs (1864; 3), Marignac (1873; 2), and finally Lebeau (1898; 8, 1899; 11) confirmed the salts and Marignac fully described the crystals of  $\text{BeF}_2 \cdot 2\text{KF}$ , but the other salt yielded no well defined crystals. Crystals of  $\text{BeF}_2 \cdot 2\text{KF}$  are readily thrown down by evaporation of a mixture of the constituents. It is soluble in 19 parts of boiling water and 50 parts of water at  $20^\circ$ . It decrepitates slightly when heated and fuses at a red heat. If large excess of  $\text{BeF}_2$  is present, a mass, having approximate composition,  $\text{BeF}_2 \cdot \text{KF}$ , is formed, which on being again crystallized yields the first named salt. Its individuality as a definite double salt seems somewhat doubtful. Klatzo (1869; 1) claims these salts can not be made, but Lebeau (1899; 11) confirms Marignac.

**Sodium Beryllium Fluorides**,  $\text{BeF}_2 \cdot \text{NaF}$ ,  $\text{BeF}_2 \cdot 2\text{NaF}$ .—Two sodium beryllium fluorides have been described by Marignac (1873; 2) and Lebeau (1899; 11), entirely analogous to the potassium salts. They were made in a similar way by the simple evaporation of their constituents, and again it is the disodium salt that is obtained most easily and in definite crystals.  $\text{BeF}_2$ .

$2\text{NaF}$  is easily obtained by evaporation in small, hard, brilliant dimorphous crystals, both forms of crystals being rhombohedral prisms, but of different angle. The salt is soluble in 68 parts of water at  $18^\circ$  and in 34 parts at  $100^\circ$ . Marignac gives drawings and measurements of the crystals of  $\text{BeF}_2 \cdot 2\text{NaF}$  and could get no definite crystals of the other salt, which like the corresponding potassium compound, seems to be of doubtful existence as a definite compound.

**Ammonium Beryllium Fluoride**,  $\text{BeF}_2 \cdot 2\text{NH}_4\text{F}$ .—First prepared by Marignac, (1873; 2) and later studied by v. Helmholtz (1893; 2) and Lebeau (1899; 11). Obtained by evaporating the constituents as small colorless needles or rhombic prisms. It is isomorphous with the corresponding potassium salt. Lebeau used it as a means to prepare pure beryllium fluoride. Marignac figures the crystals and gives full measurements.

#### DOUBLE IODIDES.

Welkow (1874; 6) obtained a *double iodide of beryllium* with *bismuth* and one with *antimony*, but was unable to separate them from the mother liquors and identify the salts.

Mosnier (1897; 7) produced a *double beryllium lead iodide* by saturating a hydriodic acid solution of beryllium iodide with lead iodide. He obtained fine yellow needles decomposed by water, the analysis of which agreed fairly well with the formula,  $\text{BeI}_2 \cdot \text{PbI}_2 \cdot 3\text{H}_2\text{O}$ , although Mosnier preferred to consider beryllium as a triad.

#### DOUBLE SULPHIDES.

Berzelius (1826; 2) reported a double sulphide with tungsten but did not identify the salt.

#### DOUBLE CYANIDES.

**Beryllium Platinum Cyanide**,  $\text{BePtCy}_4 \cdot 4\text{H}_2\text{O}$ .—Toczynski (1871; 2) made beryllium platino cyanide in gold yellow crystals by the action of beryllium sulphate on barium platino cyanide and crystallization from alcohol. Atterberg (1873; 7) confirmed his results. By mixing this with the corresponding magnesium salt and recrystallizing, Toczynski obtained crystals to which he assigned the formula,  $\text{BeMg}_2\text{Pt}_3\text{Cy}_{12} + 16\text{H}_2\text{O}$ .

**Beryllium Platibromo Cyanide**,  $\text{BePtBr}_2(\text{Cy})_4$ .—Obtained by Holtz (1873; 10) as thin plates.

#### DOUBLE SULPHATES.

**Beryllium Potassium Sulphate**,  $\text{BeSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .—This sulphate was probably first prepared by Vauquelin (1798; 2), but was first described by Awdejew (1842; 2) and later by Debray (1855; 1), Klatzo (1869; 1), Marignac (1873; 2) and Atterberg (1873; 7), all of whom agree essentially as to formula and details. It is prepared by the simple evaporation of its constituents in like proportions. The crystals are small and colorless and even Marignac was unable to determine their form. They are much more soluble in hot than in cold water. Klatzo thought they contained  $3\text{H}_2\text{O}$  when crystallized between  $-2$  and  $-3^\circ \text{C}$ .

**Beryllium Acid Potassium Sulphate**,  $\text{BeSO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 2\text{HKSO}_4 \cdot 4\text{H}_2\text{O}$ .—Atterberg (1873; 7) by evaporating a strongly acid solution of like equivalents of beryllium sulphate and potassium sulphate, obtained a mass of fine needle-shaped prisms to which he assigned the above formula.

**Sodium Beryllium Sulphate**,  $3\text{BeSO}_4 \cdot 2\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ .—Reported by Atterberg (1873; 7) as fine needle-shaped crystals forming in radiating star-shaped groups and obtained by evaporating a solution containing three equivalents of beryllium sulphate and one of sodium sulphate, to a thick syrup. Loses  $7\text{H}_2\text{O}$  at  $100^\circ$ .

**Ammonium Beryllium Sulphate**,  $\text{BeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$ .—Obtained by Atterberg (1873; 7) by evaporating like equivalents of the two sulphates first by heat and then over sulphuric acid to a thick syrup. On stirring, the syrup became a crystalline mass and by pouring out the mother liquor, he obtained the crystals to which he assigned the above formula. They lost all their water at  $110^\circ$ .

#### DOUBLE SULPHITES.

**Potassium Beryllium Sulphite**,  $2\text{BeSO}_3 \cdot \text{K}_2\text{SO}_3 \cdot 9\text{H}_2\text{O}$ .—Rosenheim and Woge (1897; 4) obtained this salt in the crystalline form by saturating acid potassium sulphite with beryllium hydroxide and after filtering, passing in excess of sulphur diox-

ide and evaporating the solution in a desiccator in an atmosphere of sulphur dioxide. No description of the salt is given other than its analysis and the fact that it lost sulphur dioxide easily when exposed to the air.

**Ammonium Beryllium Sulphite,**  $2\text{BeSO}_3 \cdot (\text{NH}_4)_2\text{SO}_3 \cdot 4\text{H}_2\text{O}$ .—Prepared by Rosenheim and Woge (1897; 4) in the same manner as the potassium salt and had similar properties. On exposure to air lost ammonium sulphite as well as sulphur dioxide.

**Sodium Beryllium Sulphite.**—Rosenheim and Woge (1897; 4) failed to prepare this salt, obtaining only an uncrystallizable syrup.

**Double Beryllium Molybdates.**—Rosenheim and Woge (1897; 4) were unable to obtain any double salt with either potassium sodium or ammonium molybdate.

#### DOUBLE NITRITE.

**Beryllium Diplatonitrite,**  $\text{BePt}(\text{NO}_2)_4 \cdot \text{PtO}_2 \cdot 9\text{H}_2\text{O}$ .—Was prepared by Nilson (1876; 3) by treating barium platonitrite with barium sulphate and evaporating in a vacuum. Obtained small bright red crystals which are probably not a true double salt, as in solutions of these salts the platinum ion is apparently not present.

**Beryllium Platino-di-iodo-nitrite.**—Prepared by Nilson (1878; 7) in the form of small, quadrangular, yellow tables which decomposed at  $100^\circ$ . Crystals were very deliquescent and very soluble in water.

#### DOUBLE PHOSPHATES.

**Potassium Beryllium Orthophosphate,**  $\text{BeKPO}_4$ .—Grandean (1886; 2) first prepared this phosphate by fusing the sulphate of beryllium with acid potassium phosphate. Ouvrard (1890; 11) by fusing beryllium oxide with either meta-, ortho- or pyrophosphate obtained the same compound in rhombic prisms.

**Sodium Beryllium Orthophosphate,**  $\text{BeNaPO}_4$  and  $\text{BeNa}_4(\text{PO}_4)_2$ .—Wallroth (1883; 1) first obtained this phosphate by fusing beryllium oxide in sodium metaphosphate. The crystals obtained were in the form of hexagonal plates. Ouvrard (1890; 11) obtained the same salt in the same manner and also by using sodium pyrophosphate. He states that his crystals were

identical with those of beryllonite. By using sodium orthophosphate instead of meta- or pyrophosphate, he obtained the second phosphate,  $\text{Na}_4\text{Be}(\text{PO}_4)_2$ , in lamellae.

**Ammonium Beryllium Phosphate.**—Rössler (1878; 9) has shown that a crystalline precipitate, similar to ammonium magnesium phosphate can be produced by adding an excess of ammonium phosphate to a beryllium salt, adding hydrochloric acid and just neutralizing with ammonia, but states that this precipitate varies in composition. M. Austin (1899; 8) has also worked with this precipitate in an attempt to obtain an analytical method for beryllium, but agrees that the results are inaccurate.

**Ammonium Sodium Beryllium Phosphate**,  $\text{Be}(\text{Na})_2(\text{NH}_4)_2(\text{PO}_4)_2$ .—Prepared according to Scheffer (1859; 3) by precipitating beryllium nitrate with sodium phosphate in the presence of ammonium chloride.

#### DOUBLE CARBONATES.

**Ammonium Beryllium Carbonate.**—By precipitating an ammonium carbonate solution of beryllium hydroxide with alcohol, a white deposit is obtained which is fairly stable and the composition of which depends upon the relative amounts of the constituents present and especially upon the mass of the carbon dioxide component. If such a solution is boiled previous to the addition of the alcohol and the latter added at the point where the beryllium begins to separate as a basic carbonate, the precipitate has the composition,  $3\text{BeCO}_3 \cdot \text{Be}(\text{OH})_2 + 3(\text{NH}_4)_2\text{CO}_3$ , according to Debray (1855; 1) and Klatzo (1869; 1), while Humridge (1886; 1) assigns to it the formula,  $2(\text{BeCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3) \cdot \text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ . This slowly loses ammonia and carbon dioxide in the cold and quickly on heating.

**Potassium Beryllium Carbonate.**—By a similar procedure to the preceding, Debray obtained a double salt or a mixture to which he assigned the analogous formula,  $3(\text{BeCO}_3 \cdot \text{K}_2\text{CO}_3) \cdot \text{Be}(\text{OH})_2$ . It was obtained in the form of a white precipitate by adding alcohol to a solution of beryllium hydroxide in potassium carbonate.



## DOUBLE SILICATES.

**Potassium Beryllium Silicate.**—Hautefeuille and Perrey (1888; 5, 1893; 1) obtained crystals of a potassium beryllium silicate of indefinite composition by fusing the constituents of a beryllium leucite in excess of potassium vanadate. They concluded that these heterogeneous crystals were mixtures of simpler types. Friedel and Sarasin (1892; 1) obtained a beryllium aluminum potassium silicate in hexagonal prisms by fusing the oxides of the first two in potassium silicate. Duboin (1896; 5) obtained crystals of a double silicate varying in composition between  $2K_2O.3BeO.5SiO_2$  and  $2K_2O.3BeO.7SiO_2$  by dissolving beryllium oxide and silicon dioxide in potassium fluoride and then submitting to long fusion with potassium chloride.

**Sodium Beryllium Silicate.**—Hautefeuille and Perrey (1890; 11 and 1893; 1) in manner analogous to their corresponding potassium compounds by fusing the constituents of a beryllium nephelene in excess of sodium vanadate, obtain crystals of a silicate varying between wide limits and which they concluded were mixtures of simpler types.

**Lithium Beryllium Silicate.**—Friedel (1901; 4) by fusing together the constituents, obtained a silicate which he considered a mixture of  $Li_2SiO_3$  and  $Be_2SiO_4$  showing an isomorphism similar to that between albite and anorthite.

**Aluminum Beryllium Silicate,  $Be_3Al_2(SiO_3)_6$ .**—Artificial beryl has been made by both Williams (1873; 3) and by Hautefeuille and Perrey (1888; 4) by fusing together the proper mixture of beryllium, aluminum and silicon oxides, the latter authors using acid lithium molybdate as a mineralizing agent. The natural color of emeralds may be given by means of chromium, using a reducing flame. Although Williams fused his beryl in the oxy-hydrogen flame, the flame is scarcely hot enough to make even fairly imitative emeralds, the necessary mixture of gases to give a clear fusion developing bubbles and oxidizing the color.

## DOUBLE OXALATES.

**Potassium Beryllium Oxalate,  $BeC_2O_4.K_2C_2O_4$ .**—Debray (1855; 1) first obtained this oxalate by evaporating the constituents together, and his work has since been corroborated by Rosenheim

and Woge (1897; 4) and Wyruboff (1902; 1). Rosenheim and Woge also obtained it with one molecule of water of crystallization. Wyruboff was unable to measure the crystals, but states that owing to its comparative insolubility it is a promising means of separating beryllium from iron and aluminum. In a later article (1902; 2) he actually uses this property to separate beryllium from beryl, precipitating by means of acid potassium oxalate.

**Potassium Diberyllium Oxalate**,  $K_2O \cdot 2BeO \cdot C_2O_3 + 2\frac{1}{3}H_2O$ . — Prepared by Philipp (1883; 2) by saturating acid potassium oxalate with beryllium hydroxide. Rosenheim and Woge (1897; 4) by the same method did not get regular results as the beryllium hydroxide dissolved varied with the condition. By saturating at the boiling point, diluting somewhat and allowing to stand the excess of beryllium hydroxide was deposited and on filtering the solution and evaporating over sulphuric acid distinct crystals separated out having the above composition.

**Sodium Beryllium Oxalate**,  $BeC_2O_4 \cdot Na_2C_2O_4 \cdot H_2O$ . — Prepared by Rosenheim and Woge (1897; 4) and by Wyruboff (1902; 1) in the same manner as the analogous potassium compound and resembling it closely. It gives off but part of its water at  $120^\circ$  and is comparatively insoluble in water.

**Sodium Diberyllium Oxalate**,  $Na_2O \cdot 2BeO \cdot 2C_2O_3 + 5H_2O$ . — Prepared by Rosenheim and Woge (1897; 4) in the same manner as the corresponding potassium salt. It differs from it in being crystallized only from much more concentrated solution.

**Ammonium Beryllium Oxalate**,  $BeC_2O_4 \cdot (NH_4)_2C_2O_4$ . — Prepared first by Debray (1855; 1) by crystallizing the constituents together from water solution and used by him in his determinations of the atomic weight of beryllium. Philipp (1883; 2) considers this salt characteristic for beryllium and of probable use in separating the element. Rosenheim and Woge (1897; 4) also produced the salt. Its analysis is about the only detail given.

**Ammonium Diberyllium Oxalate**,  $(NH_4)_2O \cdot 2BeO \cdot 2C_2O_3 \cdot 2\frac{1}{2}H_2O$ . — Prepared by Rosenheim and Woge (1897; 4) strictly analogous in composition and method of preparation to the

corresponding potassium salt. Crystallizable only from a very concentrated solution.

**Rubidium Beryllium Oxalate**,  $\text{BeC}_2\text{O}_4 \cdot \text{Rb}_2\text{C}_2\text{O}_4$ .—Prepared by Wyrouboff (1902; 1) in well defined triclinic crystals which he measured and described. Axial ratio 1.0814:1:1.2575,  $bc=78^\circ 40'$ ,  $ac=86^\circ 46'$ ,  $ab=105^\circ 40'$ . It is more readily soluble in water than the potassium or sodium salt.

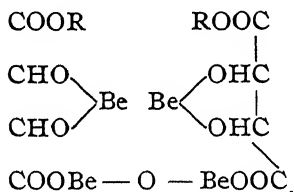
**Lithium Beryllium Oxalate**,  $\text{BeC}_2\text{O}_4 \cdot \text{Li}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ .—Prepared by Wyrouboff (1902; 1) in thin monoclinic tables which are very soluble in water and lose their water of crystallization at  $110^\circ$ . Crystals were measured 0.6163:1:1.5445,  $ac=91^\circ 42'$ .

#### DOUBLE TARTRATES.

These salts have been studied by Toczynski (1871; 2), Rosenheim and Woge (1897; 4) and Rosenheim and Itzig (1899; 13) and show some remarkable properties especially in that the beryllium appears to take the place of the hydrogen of the organic group as well as the acid hydrogen. The compounds thus obtained have exceptionally great molecular rotation. Toczynski reports two potassium beryllium tartrates,  $\text{KBe}_2\text{C}_4\text{H}_2\text{O}_6 + \text{Aq}$  and  $\text{KBe}_2\text{C}_4\text{H}_2\text{O}_6 + \text{Aq}$ . The first separated in small spheres after crystallizing out some tartaric acid from a mixture of two molecules of acid potassium tartrate and one molecule of beryllium hydrate. The second crystallized in hemimorphous prisms from solution of acid potassium tartrate saturated by boiling with excess of beryllium hydroxide. It should be identical with the potassium diberyllium tartrate of Rosenheim and Woge. Toczynski also obtained some glassy uncrystallizable masses of antimony beryllium tartrate by treating tartaric acid with antimony and beryllium oxides, but they were too indefinite to be given place among the compounds of beryllium.

The double tartrates of beryllium and the alkalis have been made the subject of an extended research by Rosenheim and Woge (1897; 4) and Rosenheim and Itzig (1899; 13) and have been carefully systematized by these authors. According to them beryllium forms two series of compounds with the alkalis, the monoberyllium alkali tartrates and the diberyllium alkali tartrates.

**Diberyllium Alkali Tartrates**,  $K_2Be_4C_8H_4O_{13} + 7H_2O$ ,  $Na_2Be_4C_8H_4O_{13} + 10H_2O$ ,  $(NH_4)_2Be_4C_8H_4O_{13} + 10H_2O$ .—These salts are obtained as beautiful large crystals by saturating the corresponding bitartrate with freshly precipitated beryllium hydroxide and evaporating to crystallization. On recrystallizing several times, the salts were obtained pure and agreed empirically with the above formulas. The authors believe, however, from the molecular rotation and molecular conductivity of these salts that they contain the complex anion,  $Be_4C_8H_4O_{13}^{==}$  and are in reality compounds similar to the copper and lead tartrates described by Kahlenberg (Ztschr. phys. Chem., 17, 577), having a double molecular formula corresponding to



In their opinion the salts are largely dissociated even in comparatively concentrated solution, and the complex anion is unusually stable and subject but little to hydrolysis as the molecular rotation changes but little on dilution. They found the molecular rotation of these salts extraordinarily high. They were calculated on the basis of the water free simplest formulas.

$$KBe_2C_4H_2O_7 = + 225.3$$

$$NaBe_2C_4H_2O_7 = + 225.1$$

$$NH_4Be_2C_4H_2O_7 = + 241.7.$$

Also the molecular conductivity was determined

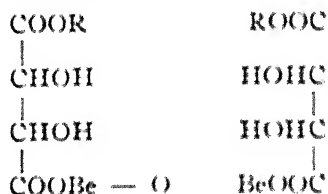
$$\frac{1}{2}(K_2Be_4C_8H_4O_{13} + 7H_2O), \Delta = \mu_{1024} - \mu_{32} = 63.9 - 43.6 = 20.3,$$

$$\frac{1}{2}(Na_2Be_4C_8H_4O_{13} + 10H_2O), \Delta = \mu_{1024} - \mu_{32} = 59.3 - 38.6 = 20.7.$$

They made no migration tests for the presence of the anion.

**Monoberyllium Alkali Tartrates**,  $K_2Be_2C_8H_8O_{13} + 2H_2O$ ,  $(NH_4)_2Be_2C_8H_8O_{13} + 2H_2O$ ,  $Na_2Be_2C_8H_8O_{13} + 3H_2O$ , are rather more indefinite than the diberyllium salts as they are not obtained as distinct crystals. By treating a slight excess of alkali bitartrate with the calculated amount of beryllium hydrox-

ide, boiling and concentration, the excess of alkali tartrate crystallizes out and on further evaporation a thick syrup is obtained, which on cooling solidifies to a mass of apparently constant composition. The authors assign the double formula also to these residues corresponding with the type



and believe it contains the complex anion,  $\text{Be}_2\text{C}_4\text{H}_4\text{O}_{11}$ . This anion like that of the diberyllium salts is very stable and not hydrolyzed on dilution. The molecular rotation was determined for the potassium and ammonium salts only as they were not able to obtain the sodium salt in sufficient quantity free from excess of bitartrate. The results of many closely agreeing determinations in solutions of varying dilution yielded for the molecular rotation, calculated on the water free molecule,

$$\begin{array}{ll}
 \frac{1}{2} (\text{K}_2\text{Be}_2\text{C}_4\text{H}_4\text{O}_{11}) & 124.7^\circ \\
 \frac{1}{2} ((\text{NH}_4)_2\text{Be}_2\text{C}_4\text{H}_4\text{O}_{11}) & 125.8^\circ
 \end{array}$$

**Ammonium Diberyllium Racemate**,  $(\text{NH}_4)_2\text{Be}_2\text{C}_4\text{H}_4\text{O}_{11} + 10\text{H}_2\text{O}$ ; **Ammonium Monoberyllium Racemate**,  $(\text{NH}_4)_2\text{Be}_2\text{C}_4\text{H}_4\text{O}_{11} + 2\text{H}_2\text{O}$ .—These two salts were also prepared by Rosenheim and Itzig (1899; 13) and were found to be in every way analogous to the corresponding tartrates except, as was to be expected, they were optically inactive. This of course shows that beryllium has the same effect of increasing the regular rotation when substituted in the molecule of the laevo-tartrates as has been shown to be the case with the dextro-tartrates.

The result of the introduction of beryllium into the tartrate molecule is well shown by the following table:

	MOLECULAR ROTATION $[\text{M}]_D$ OF			
	Bitartrate	Tartrate	Monoberyllium Tartrate	Diberyllium Tartrate
Ammonium.....	+ 42.8°	+ 63.0°	+ 125.8°	+ 241.7°
Potassium.....	42.5°	64.4°	124.7°	225.3°
Sodium.....	41.2°	59.9°		225.1°

## DOUBLE MALATES.

Rosenheim and Itzig (1899; 13) by saturating laevo-alkali acid malates with freshly precipitated beryllium hydroxide at boiling temperature, obtained excellently crystallized diberyllium malates in small prismatic crystals. These crystals were much less soluble in water than the corresponding tartrates and consequently separated from comparatively dilute solution. They prepared

**Potassium Diberyllium Malate**,  $K_2Be_4C_8H_6O_{12} + 5H_2O$ .

**Sodium Diberyllium Malate**,  $Na_2Be_4C_8H_6O_{12} + 7H_2O$ .

**Ammonium Diberyllium Malate**,  $(NH_4)_2Be_4C_8H_6O_{12} + 4H_2O$ .

By precipitating any one of these salts with dilute barium chloride solution, a precipitate formed of needle-shaped crystals of

**Barium Diberyllium Malate**,  $BaBe_4C_8H_6O_{12} + 6$  or  $12H_2O$ .—

The precipitation of this salt seems to lend additional evidence of the existence of these complex tartrates and malates as definite compounds. Mercury, lead and silver salts threw down only amorphous precipitates.

Rosenheim and Itzig determined the molecular rotation

$$\frac{1}{2}(K_2Be_4C_8H_6O_{12}) = 198.9^\circ,$$

$$\frac{1}{2}(Na_2Be_4C_8H_6O_{12}) = 202.2^\circ,$$

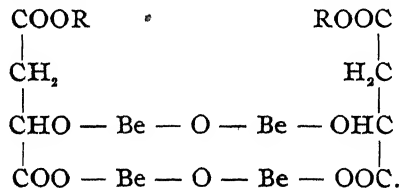
$$\frac{1}{2}(NH_4Be_4C_8H_6O_{12}) = 200.9^\circ.$$

They also determined the molecular conductivity and found for

$$\frac{1}{2}(K_2Be_4C_8H_6O_{12}), \Delta = \mu_{1024} - \mu_{32} = 63.8 - 45.5 = 18.3,$$

$$\frac{1}{2}(Na_2Be_4C_8H_6O_{12}), \Delta = \mu_{1024} - \mu_{32} = 55.5 - 36.2 = 19.3.$$

They argue that these salts contain the stable anion,  $Be_4C_8H_6O_{12}$ , and that the molecule is structurally according to the type



**Ammonium Monoberyllium Malate**,  $(NH_4)_2Be_2C_8H_8O_{11} + H_2O$ .

—This salt was also prepared and studied by Rosenheim and

Itzig (1899; 13) by the same method as used for the corresponding tartrate. The sodium and potassium salts could not be separated from an excess of bimalate. The salt was obtained simply as a non-crystalline mass left on evaporation. By analysis this mass corresponded to the formula given above. The molecular rotation was determined and found for  $\frac{1}{2}(\text{NH}_4)_2\text{Be}_2\text{C}_8\text{H}_8\text{O}_{11}$  to be  $106.3^\circ$ .

The strong influence which beryllium exerts upon the polarization of the malates is shown by the following table:

MOLECULAR ROTATION $[\text{M}]_D$ .				
	Bimalate	Neutral Malate	Monoberyllium Malate	Diberyllium Malate
Ammonium.....	— 9.89	— 13.27	— 106.3	— 200.9
Potassium .....	— 9.68	— 14.26		— 198.9
Sodium.....	— 10.02	— 14.31		— 202.2

## CHAPTER VI

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### BASIC COMPOUNDS OF BERYLLIUM.

Some of the most interesting problems of the chemistry of beryllium lie in the equilibrium relations between its oxide and the various acid radicals. It is certainly true that many of these acids can hold in solution phenomenally large amounts of beryllium oxide extending in the case of the acetate to six equivalents (Ordway, 1858; 1), while the chloride can hold four, the sulphate three and the oxalate nearly three equivalents. These solutions on being diluted with water throw down precipitates of a highly basic nature or on evaporation leave gummy masses, the basicity of which depends upon the concentration of the acid used which determines the amount of dissolved oxide, or rather hydroxide, while they differ physically but little. Both the precipitated bodies and the residues of evaporation are amorphous and glassy in structure and vary widely in composition according to the concentration of the solutions from which they were precipitated and the extent to which the acid had dissolved the base. The basic precipitates on washing with water approach the hydroxide in composition, although the last traces of the acid radical are almost impossible to remove. These facts have given rise in literature to a large number of so-called compounds of beryllium which in reality have no existence as independent individuals, but were obtained by the analysis of the indefinite mixture or solid solution which the particular conditions happened to yield, and in many cases, indeed, have no further basis for individuality than the per cent. of  $\text{BeO}$  they were found to contain. Equilibrium experiments, or repeated crystallization without change of composition, are necessary to establish the identity of individuals, for freezing point determinations may lead to erroneous conclusions since the addition of  $\text{Be}(\text{OH})_2$  to solutions of the normal salt *raises* their freezing point (1907; 10 and 11).



It is indeed difficult to understand how the solution of the normal sulphate and nitrate can dissolve several equivalents of their own hydroxide, attack metals and carbonates almost as if they were sulphuric or nitric acid themselves, yielding these basic substances and still be less hydrolyzed (Leys, 1899; 1, Brunner, 1900; 1) than the corresponding salts of iron and aluminum. Certainly it seems to be true that all of the so-called basic compounds of beryllium, produced in the presence of water by adding the hydroxide or basic carbonate to a solution of an acid or a normal salt, have no real existence as such, but come only in the domain of homogeneous phases of variable composition. To this some double salts, especially the tartrates and malates of Rosenheim and Itzig (1899; 13), may seem to be an exception, for at least some of them are obtained crystalline and of apparent definite composition. It must not be forgotten, however, that the authors claim these to be not basic in nature, but complex and that the excess of beryllium replaces hydrogen in the acid radical, giving rise to complex anions to which their abnormal optical properties are due.

In contradistinction to the above substance we have, however, the truly phenominal and actually basic compounds of beryllium which are produced pure, only in contact with anhydrous acid or so nearly anhydrous that the mass of the water present becomes negligible to produce hydrolysis. The true basic compounds so far obtained belong solely to the fatty acid series. Their solubility increases with the molecular weight.

**Basic Beryllium Acetate**,  $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$ .—This unique and interesting chemical compound appears to be peculiar to beryllium alone. It was discovered by Urbain and Lacombe (1901; 2) who studied it and described its properties. Parsons (1904; 5) used it as a means of determining the atomic weight of beryllium. Haber and Van Oordt (1904; 4) used its solubility in chloroform as a means of separating and purifying beryllium compounds, and Parsons (1904; 5) and Parsons and Robertson (1906; 1) used its property of ready crystallization from hot glacial acetic acid for the same purpose.

Basic beryllium acetate melts at  $283^{\circ}$ - $284^{\circ}$  and boils at  $330^{\circ}$ - $331^{\circ}$ , and is readily sublimed without decomposition. It has a vapor density agreeing with the formula,  $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_2$ . It is itself almost insoluble in water, but is slowly hydrolyzed by cold water and quickly by hot, after which it dissolves. It is easily soluble in absolute alcohol and in chloroform, and is soluble in benzene, toluene, xylene, naphtha and all petroleum distillates, turpentine, methyl alcohol, amyl alcohol, ether, ethyl acetate, acetone and carbon disulphide. It is also soluble in acetic anhydride and glacial acetic acid and is only converted to the normal salt by a mixture of these reagents on heating to  $150^{\circ}$  in a closed tube (Steinmetz, 1907; 5). Although a basic compound, its solution in glacial acetic acid can be saturated with hydrochloric acid gas and remain unchanged. It is unaffected in dry air. Ordinary acids attack it setting free acetic acid, probably through the agency of water they contain. It is much more soluble in boiling glacial acetic acid than in cold and is most readily crystallized in this manner. On cooling, it separates from boiling glacial acetic acid as small shining grains which, under a magnifying glass, are seen to be almost perfect octahedrons. The specific gravity of the basic acetate is 1.362 referred to water at  $4^{\circ}$  (Parsons, 1904; 5). It is best prepared by dissolving the carbonate or hydroxide in acetic acid, evaporating off all water and drying the residue. The residue is then boiled in pure glacial acetic acid which dissolves it completely and on cooling a mass of small glistening octahedral crystals of the basic acetate are deposited. These may be recrystallized from hot acid as many times as desired.

Vauquelin (1798; 5) and Ordway (1858; 1) both attempted to make the acetate of beryllium but obtained the ordinary gummy form through not being able to understand the fact that the presence of water made its preparation impossible.

Tanatar (1904; 3) also studied the basic acetate and concluded that its peculiar properties led to the supposition that beryllium is a tetravalent element with an atomic weight of 18.2. His belief is apparently not shared by others as the valency of

beryllium was long ago established from the vapor density of the chloride and bromide.

**Basic Beryllium Formate**,  $\text{Be}_4\text{O}(\text{CHO}_2)_6$ .—This compound was first prepared by Lacombe (1902; 3) by the action of anhydrous formic acid in excess on the carbonate and sublimation of the product under diminished pressure. Parsons (1904; 5) attempted to use it for atomic weight determination, but found its sublimation and purification too difficult, as even under much diminished pressure it was partly decomposed.

According to Lacombe it is insoluble in all solvents and as it sublimes without fusion, he did not determine its melting or boiling point. Tanatar (1907; 12) claimed to make it by mixing the calculated amounts of carbonate and acid and boiling in water, which is impossible.

**Basic Beryllium Propionate**,  $\text{Be}_4\text{O}(\text{C}_3\text{H}_5\text{O}_2)_6$ .—Was prepared by Lacombe (1902; 3) in the same way as the acetate. It is a solid having a melting point of  $119^\circ$ - $120^\circ$  and a boiling point of  $339^\circ$ - $341^\circ$ . It sublimes at  $221^\circ$  under 19 millimeters pressure. No other details given. Tanatar (1907; 12) by treating with acetyl chloride obtained crystals of  $\text{Be}_4\text{O}(\text{C}_3\text{H}_5\text{O}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_3$  with melting point  $127^\circ$  and boiling point  $330^\circ$ . Boiling without decomposition. Soluble in ether and benzene.

**Basic Beryllium Isobutyrate**,  $\text{Be}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_6$ .—Prepared by Lacombe (1902; 3) in manner analogous to the acetate, is a solid melting at  $76^\circ$  and boiling at  $336^\circ$ - $337^\circ$ . Under 19 millimeters pressure it sublimes at  $216^\circ$ . No other details given.

**Basic Beryllium Butyrate**,  $\text{Be}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_6$ .—Is a liquid prepared in the same way as the acetate by Lacombe (1902; 3) which boils at  $239^\circ$  under 19 millimeters pressure. No other details given. Tanatar (1907; 12), by treating this with acetyl chloride, obtained  $\text{Be}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_4(\text{C}_2\text{H}_3\text{O}_2)_2$  a liquid soluble in benzene and ether, melting at  $-15^\circ$  and boiling at  $351^\circ$ .

**Basic Beryllium Isovalerianate**,  $\text{Be}_4\text{O}(\text{C}_5\text{H}_9\text{O}_2)_6$ .—Is a liquid prepared by Lacombe (1902; 3) in the same way as the acetate. It boils at  $254^\circ$  under 19 millimeters pressure. No other details given.

**INDEFINITE BASIC BERYLLIUM SOLID PHASES.**

Among the basic beryllium substances which are of variable composition, but to which formulas have been assigned, the sulphates, oxalates and carbonates have been most studied and in the first two cases they have been shown to be simply solid solutions of the hydroxide and the normal salt. These three only are worthy of separate mention.

**BASIC SULPHATES.**

Berzelius (1815; 1) first showed that beryllium sulphate dissolves its own hydroxide in quantity although Vauquelin (1808; 5) and Gmelin (1801; 1) had already produced a gummy sulphate. Berzelius assigned the formulas,  $3\text{BeO} \cdot \text{SO}_3$  and  $2\text{BeO} \cdot \text{SO}_3$ , to the evaporated residue of the corresponding solution for no other apparent reason than that they represented whole equivalents, although he must have known that any intermediate ratio between  $3\text{BeO} \cdot \text{SO}_3$  and  $\text{BeO} \cdot \text{SO}_3$  was as easily obtained and that any one of these residues had as good claim to the dignity of being a compound. To the basic precipitate obtained by diluting the concentrated solution of  $3\text{BeO} \cdot \text{SO}_3$  with water, Berzelius gave the formula,  $6\text{BeO} \cdot \text{SO}_3 \cdot 3\text{H}_2\text{O}$ . Debray (1855; 1), many years later, used these basic sulphates as a method of separation from aluminum but assigned no formulas. Atterberg (1873; 7) also obtained precipitates by diluting with water the strong solution of  $\text{BeSO}_4$  saturated with  $\text{Be}(\text{OH})_2$  and assigned formulas,  $\text{BeSO}_4 \cdot 5\text{Be}(\text{OH})_2 + 2\text{H}_2\text{O}$  and  $\text{BeSO}_4 \cdot 7\text{Be}(\text{OH})_2 + \text{H}_2\text{O}$ . He also again evaporated solutions containing three and two equivalents of the oxide to one of acid and of course obtained residues of that ratio corresponding to the first two formulas assigned by Berzelius. Parsons (1904; 10) attacked this problem by means of equilibrium experiments in a large specially constructed thermostat and showed that the precipitates obtained by diluting the more basic solutions consisted of a single phase, that they had a ratio when equilibrium was reached as high as  $25\text{BeO}$  to  $1\text{SO}_3$ , that they varied in composition and that, therefore, they could only be a solid solution of the hydroxide containing a small amount of the normal salt. He also studied the basic liquid solution and showed that there

was nothing characteristic in the residue obtained by evaporating any particular ratio of acid to base.

Parsons and Robinson and Fuller (1906; 3, 1907; 10) again took up the question of the solution of  $\text{Be}(\text{OH})_2$  in  $\text{BeSO}_4$  solution and showed that the freezing point was raised and the conductivity lowered thereby, and that no anion containing beryllium was formed. They also showed that on dialyzing such solutions into water, beryllium hydroxide invariably separated out and the solution left behind always had a higher basic ratio than that which had passed through the parchment.

All these facts prove that none of these substances are true compounds, but merely solutions of some form or other. It seems quite probable that beryllium sulphate once dissolved acts simply as a liquid in which its own hydroxide is soluble (1907; 11).

#### BASIC OXALATES.

These substances hold a strictly analogous position to the sulphates already mentioned. Vauquelin (1798; 5) and Debray (1855; 1) had obtained simply gummy basic masses and apparently realizing that they were not true compounds gave them no formulas. Atterberg (1873; 7) had the same experience, but assigned the formula,  $\text{BeC}_2\text{O}_4 \cdot \text{Be}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , to the mass obtained by evaporating the solution of one equivalent of the hydroxide in one equivalent of the normal oxalate and the formula,  $\text{BeC}_2\text{O}_4 \cdot 6\text{Be}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ , to the highly basic precipitate obtained by diluting the solution of the first with a large excess of water. Parsons and Robinson (1906; 1) studied these basic oxalates by phase rule considerations, by the same method as had been used on the basic sulphates and showed that when equilibrium was reached the precipitated basic oxalates had a ratio as high as  $25\text{BeO}$  to  $1\text{C}_2\text{O}_4$ , that they varied in composition, that they consisted of a single phase and must, therefore, be simply a solid solution of the oxalate in the hydroxide or the simple hydroxide occluding some of the normal salt. The basic solutions like the sulphate appear to be a case of simple solution of the hydroxide in a mixed solvent consisting of water and beryllium oxalate. When the concentration of beryllium ox-

alate in such a solution reaches its maximum, it will dissolve 1.85 equivalents of beryllium hydroxide.

#### BASIC CARBONATE.

When salts of beryllium are precipitated with sodium or potassium carbonates or when an ammonium carbonate or sodium bicarbonate solution of beryllium hydroxide is boiled, a highly basic precipitate is thrown down to which the following formulas have been assigned.

$2\text{BeCO}_3 \cdot 7\text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , (Schaffgotsch, 1840; 2).  $2\text{BeCO}_3 \cdot 7\text{Be}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$  and  $4\text{BeCO}_3 \cdot 8\text{Be}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$  (Weeren, 1854; 1).  $\text{BeCO}_3 \cdot 2\text{Be}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ , (Debray, 1855; 1), (Klatzo, 1860; 1).  $\text{BeCO}_3 \cdot 2\text{Be}(\text{OH})_2 \cdot \text{Aq}$  (Parkman, 1862; 1).  $\text{BeCO}_3 \cdot 5\text{Be}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ , (Seubert and Elten 1893; 4).  $\text{BeCO}_3 \cdot 2\text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , (Pollok, 1904; 1).

These formulas represent little else than an approximation at equilibrium between  $\text{BeO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$  under the conditions present. In the presence of the largest possible amount of the carbon dioxide the composition is approximately represented by one equivalent of the carbonate to two of the hydroxide, but boiling which not only increases hydrolysis, but removes carbon dioxide from the system, slowly causes the solid phase to approach the pure hydroxide. There is nothing in literature to indicate that anyone of the intermediate stages represents a true compound and this is apparently realized by one or two of the authors.

Chemically the basic precipitate is much the same whether it is thrown down by a soluble carbonate or by boiling an ammonium carbonate or diluted acid sodium carbonate solution. In either case it occludes notable quantities of the precipitant, which can not be removed by washing and the author has never found less than two per cent. so contained. This fact is not generally realized, but is of decided importance when this substance is to be used as a basis for the preparation of other compounds. In the case of occluded ammonia it can be removed by prolonged boiling or by intermittently passing carbon dioxide through the precipitate suspended in water, filtering off the liquid and repeating. Many hours boiling is required by the first procedure and the residue left is almost the pure

hydroxide, while if the second method is used the purification is a matter of days, but the residue is about as rich in the  $\text{CO}_2$  component as when first precipitated. Passing carbon dioxide through the boiling liquid has little effect on the result as would naturally be expected. The ammonia may be removed with but little loss of carbon dioxide, by momentarily boiling with steam, filtering, addition of fresh cold water and repeating several times. Ordinary washing with hot water does not seem to be effective. Drying at  $100^\circ$  does not remove the occluded ammonia, but its odor becomes immediately apparent on heating to the point where the carbon dioxide begins to be evolved.

Physically the precipitates thrown down by alkaline carbonates are quite different from the precipitate on boiling an ammonium carbonate solution; the first being gelatinous and difficult to wash while the latter comes down in granular condition and filters most readily. A saturated solution of ammonium carbonate will dissolve an amount of freshly precipitated beryllium carbonate or hydroxide equivalent to 22 grams  $\text{BeO}$  in 1000 cubic centimeters (Pollak, 1904; 1). On boiling this solution, carbon dioxide and ammonia escape rapidly and soon the basic carbonate precipitate begins to appear in fine white granular form. The boiling is best done by means of steam as otherwise very violent bumping takes place which continuous stirring will not entirely prevent. The first portions of the precipitate thrown down by boiling a solution saturated with ammonium carbonate are rather richer in carbon dioxide than those that follow having a composition approximating  $\text{BeCO}_3 \cdot \text{BeCO}_3 \cdot 5\text{Be(OH)}_2 \cdot 3\text{H}_2\text{O}$  (Seubert and Elten 1893; 4).  $\text{BeCO}_3$ , the boiling is continued in such a solution until precipitation is complete the composition is approximately  $\text{BeCO}_3 \cdot 2\text{H}_2\text{O}$  (Parsons, 1904; 5). If, on the other hand, the solution is diluted, some four or five times hydrolysis of the whole material present takes place with very little boiling, and the granular carbonate thrown down appears to have the approximate composition  $\text{BeCO}_3 \cdot 2\text{Be(OH)}_2 \cdot 4\text{Aq}$ . This material can be dried at  $150^\circ$  without notable loss of carbon dioxide. Further boiling causes gradual loss of carbon dioxide and eventual-

ly only the hydroxide is left. Attempts by the writer to increase the carbon dioxide component in the precipitate, beyond that already indicated by passing the gas under pressure over the precipitate and also over freshly precipitated hydroxide have so far proven unavailing.

The basic carbonate obtained by boiling the ammonium carbonate solution, while of no definite composition, is quite properly a favorite material to be used as a basis for the production of beryllium salts since it dissolves readily in acids and if care is taken to remove all the occluded ammonia a pure salt is obtained at once. Acid sodium carbonate is an equally good solvent and on diluting a saturated solution some four or five times and boiling the basic carbonate is thrown down, but is more difficult to obtain in granular form. The occluded sodium carbonate moreover can not, of course, be volatilized off.

#### MISCELLANEOUS BASIC SOLID PHASES.

Besides the basic sulphates, oxalates and carbonates, already enumerated, many other gummy precipitates and residues of evaporation have been assigned formulas as definite compounds and find place in the literature of beryllium. They are all prepared in much the same way and generally by saturating the solution of an acid or of a normal salt with beryllium hydroxide or carbonate and by evaporation or diluting with water obtaining a solid phase which is generally more or less changed by further washing with water. In the opinion of the writer none of these "so-called" compounds, appearing in literature, of which the following is a list, have any proven claim for individual existence, but are in reality solid solutions of the normal salt with the hydroxide or, what is much the same thing, the hydroxide with more or less occluded normal salt.

##### *Basic sulphites:*

$2\text{BeSO}_3 \cdot 9\text{Be}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ , Seubert and Elten, 1893; 4.

$\text{BeSO}_3 \cdot \text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , Atterberg, 1873; 7.

$\text{BeSO}_3 \cdot \text{Be}(\text{OH})_2 \cdot \text{Aq}$ , Krüss and Moraht, 1890; 4.

$3\text{BeSO}_4 \cdot \text{Be}(\text{OH})_2 \cdot \text{Aq}$  " " " "

##### *Basic Dithionate:*

$2\text{BeS}_2\text{O}_6 \cdot 3\text{Be}(\text{OH})_2 + 14\text{H}_2\text{O}$ , Klüss, 1888; 2.



*Basic chlorides:*

- $3\text{BeCl}_2 \cdot 2\text{Be}(\text{OH})_2$ , Atterberg, 1873; 7.  
 $\text{BeCl}_2 \cdot 3\text{Be}(\text{OH})_2$ , Atterberg, 1873; 7.  
 $\text{BeCl}_2 \cdot 12\text{Be}(\text{OH})_2 + 10\text{H}_2\text{O}$ , Atterberg, 1873; 7.  
 $\text{BeCl}_2 \cdot 12\text{Be}(\text{OH})_2 + 4\text{H}_2\text{O}$ , Atterberg, 1873; 7.  
 $\text{Be}(\text{OH})\text{Cl}$ , Atterberg, 1875; 4.

*Basic selenites:*

- $2\text{BeSeO}_3 \cdot \text{Be}(\text{OH})_2 + 2\text{H}_2\text{O}$ , Atterberg, 1873; 7.  
 $\text{BeSeO}_3 \cdot \text{Be}(\text{OH})_2 \cdot \text{H}_2\text{O}$ , Atterberg, 1873; 7.  
 $2\text{BeSeO}_3 \cdot 3\text{Be}(\text{OH})_2 \cdot 7\text{H}_2\text{O}$ , Nilson, 1875; 2.

*Basic borates:*

- $\text{Be}(\text{BO}_2)_2 \cdot 2\text{Be}(\text{OH})_2 + \text{Aq}$ , Kruss and Moralt, 1890; 4.

*Basic nitrate:*

- $\text{Be}(\text{NO}_3)_2 \cdot \text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , Ordway, 1858; 1.

*Basic chromate:*

- $\text{BeCrO}_4 \cdot 13\text{Be}(\text{OH})_2 + 10\text{H}_2\text{O}$ , Atterberg, 1873; 7.  
 $\text{BeCrO}_4 \cdot 6\text{Be}(\text{OH})_2$ , Glassmann, 1907; 4.

*Basic molybdate:*

- $\text{BeMoO}_4 \cdot \text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ , Atterberg, 1873; 7.

*Basic succinate:*

- $\text{Be}_2\text{C}_4\text{H}_4\text{O}_4 \cdot \text{Be}(\text{OH})_2 + 2\text{H}_2\text{O}$ , Atterberg, 1873; 7.

*Basic ferrocyanide:*

- $\text{Be}_2\text{FeCy}_6 \cdot 4\text{Be}(\text{OH})_2 + 7\text{H}_2\text{O}$ , Atterberg, 1873; 7.

Also basic salts of the formula  $\text{Be}_4\text{O}(\text{Ac})_6$  or  $\text{Be}_4\text{O}(\text{Ac})_2$  claimed to be obtained by adding the carbonate to aqueous solution of the acid and evaporating.

*Basic crotonate:*

- $\text{Be}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_6$ , Tanatar (1907, 12).

*Basic isocrotonate:*

- $\text{Be}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_6$ ; Tanatar (1907, 12)

*Basic lactulinate:*

- $\text{Be}_4\text{O}(\text{C}_5\text{H}_7\text{O}_3)_6$ , Tanatar (1907; 12)

*Basic succinate:*

- $\text{Be}_4\text{O}(\text{C}_4\text{H}_4\text{O}_4)_2$ , Tanatar (1907, 12)

*Basic cyanacetate:*

- $\text{Be}_4\text{O}(\text{C}_2\text{H}_2\text{CNO}_2)_6$ , Glassmann, (1908; 1).

*Basic dichloracetate:*

$\text{Be}_4\text{O}(\text{C}_2\text{HCl}_2\text{O}_2)_6$ , Glassmann, (1908; 1).

*Basic monochloracetate:*

$\text{Be}_4\text{O}(\text{C}_2\text{H}_2\text{ClO}_2)_6$ , Glassmann, (1908; 1).

*Basic monobromacetate:*

$\text{Be}_4\text{O}(\text{C}_2\text{H}_2\text{BrO}_2)_6$ , Glassmann, (1908; 1).

*Basic monobrompropionate:*

$\text{Be}_4\text{O}(\text{C}_3\text{H}_4\text{BrO}_2)_6$ , Glassmann, (1908; 1).

*Basic lactate:*

$\text{Be}_2\text{O}(\text{C}_3\text{H}_5\text{O}_3)_2 \cdot \text{H}_2\text{O}$ , Glassmann, (1908; 1).

*Basic glycolate:*

$\text{Be}_2\text{O}(\text{C}_2\text{H}_3\text{O}_3)_2 \cdot \text{H}_2\text{O}$ , Glassmann, 1908; 1).

*Basic trichloracetate:*

$\text{Be}_2\text{O}(\text{C}_2\text{Cl}_3\text{O}_2)_2$ , Glassmann, (1908; 1).

*Basic ethylglycolate:*

$\text{Be}_2\text{O}(\text{C}_2\text{H}_5\text{C}_2\text{H}_2\text{O}_3)_2 \cdot \text{H}_2\text{O}$ , Glassmann, (1908; 1).

*Basic phenylglycolate:*

$\text{Be}_2\text{O}(\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{O}_3)_2$ , Glassmann, (1908; 1).

*Basic chloropropionate:*

$\text{Be}_2\text{O}(\text{C}_3\text{H}_4\text{ClO}_2)_2 \cdot \text{H}_2\text{O}$ , Glassman, (1908; 1).

*Basic salicylate:*

$\text{Be}_2\text{O}(\text{C}_7\text{H}_5\text{O}_3)_2$ , Glassmann, (1908; 1).

*Basic beryllium chlorides* (Vauquelin, 1798; 5, Gmelin, 1801; 1), *Nitrates* (Vauquelin, 1798; 6, Gmelin, 1801; 1). *Hypophosphites* (Rose, 1828; 1), *Valerates* (Trommsdorff, 1833; 1), *Oxalates, citrates, tartrates and acetates* (Vauquelin 1798; 5) to which no formulas were assigned nor analyses made.

## PART II.

### BIBLIOGRAPHY OF BERYLLIUM.

- 1798; 1. Vauquelin, L. N. De l'Aigue marine, ou Béril; et découverte d'une terre nouvelle dans cette pierre.  
Read at the Institute 26 Pluviose, An 6 (Feb. 14, 1808). Announces the discovery of a new earth, "la terre du Béril," separated from aluminum by the precipitation of  $\text{Be}(\text{OH})_2$  from  $\text{KOH}$  solution on boiling. Differs from aluminum in its salts being sweet, having a greater affinity for acids, giving no alum, soluble in  $(\text{NH}_4)_2\text{CO}_3$ , soluble and not being precipitated by  $\text{K}_2\text{C}_2\text{O}_4$  or  $\text{K}_2\text{C}_4\text{H}_4\text{O}_6$ . Editors suggest name "glucine" in foot note.  
Ann. de chim., **26** (1798) 155-170.  
Allg. J. Chem., **1**, (1798) 341.  
Nicholson's J., **2**, 358.  
Chem. Ann. (Crell), **14**, 422.
- 1798; 2. Vauquelin, L. N. Sur la terre du Béril; pour servir au premier mémoire sur le même objet.  
Studies new earth and gives following specific characters, sweet and astringent salts, very soluble in  $\text{H}_2\text{SO}_4$ , decomposes salts of aluminum, soluble in  $\text{NH}_4\text{OH}$ , affinity for acids between magnesium and aluminum, soluble in fixed alkalis, infusible, soluble in acids except carbonic and phosphoric, fusible with borax, absorbs one fourth of its weight of  $\text{CO}_2$ , not precipitated by saturated hydrosulphides.  
Ann. de chim., **26**, 170-177.  
Nicholson's J., **2**, 393.  
Chem. Ann. (Crell), **14**, 434.
- 1798; 3. Vauquelin, L. N. Same as 1798; 1. Again read before the French Society of Mines, and Vauquelin, in a foot note, refers to the proposed name glucine, but does not adopt it in text.  
J. des mines, **8**, 553-564.

- 1798; 4. Vauquelin, L. N. Analyse de l'émeraude du Péron. Shows identity of beryl and emerald and uses word glucine for first time, saying "on a donné le nom de glucine."  
Ann. de chim., 26, 259.  
Allg. J. Chem. (Scherer), 1, 361.
- 1798; 5. Vauquelin, L. N. Ueber die Verhältnisse der Glucine zu den Sauerem.  
Made sulphate, nitrate, chloride, phosphate, carbonate, citrate, tartrate, acetate, mostly in gummy basic masses. Purified from iron by means of KHS.  
Allg. J. Chem. (Scherer), 1, 590-596.
- 1799; 1. Vauquelin, L. N. Sur l'analyse des pierres en général et résultats de plusieurs de ces analyses faites au laboratoire de l'école des mines depuis quelques mois. Points out how to recognize beryllium in rocks.  
Ann. de chim., 30, 82.
- 1799; 2. Vauquelin, L. N. Anleitung zur Zerlegung der Fossilien.  
Allg. J. Chem. (Scherer), 3, 430.
- 1799; 3. Link, H. F. "Correspondence." Objects to name glucine because it resembles glycine, already in use.  
Allg. J. Chem. (Scherer), 3, 603.
- 1800; 1. Klaproth, M. H. In the third volume, page 78 of his Beiträge Zur Kenntniss der Mineralkörper, he refers to a paper read by himself before the royal Academy of Sciences of Berlin on Sept. 11, 1800, in which he argues against the name "Glycine," proposed for Vauquelin's earth, on the ground that sweetness is not unique to that element, but is also possessed by the yttrium earth and further is too much like "Glycine" which Link had already pointed out. Claims "Beryllerde" should be used.
- 1801; 1. Gmelin, H. R. Zerlegung des Berylls von Nertschink in Sibirien und Prüfung der daraus erhaltenen Süsserde.

Confirms Vanquelin's discovery. Short unimportant study of nitrate, chloride and sulphate.

Chem. Ann. (Crell), 17, 89.

- 1801; 2. Schaub, T. Chemische Untersuchung des blauen siberischen Berills.

Fuses beryl with NaOH and KOH in silver crucible. Confirms Vanquelin's discovery.

Chem. Ann. (Crell), 17, 174.

- 1802; 1. Ekeberg, A. G. Sur quelques propriétés de l'yttria comparés avec celles de la glucine.

Beryllium is precipitated from solution by the succinates, colorless salts, soluble in KOH, and not precipitated by alkaline prussates. Chief differences from yttria. Specific gravity  $\text{BeO}$  2.007.

J. des mines, 12, 245.

- 1809; 1. Davy, Humphrey. On some new electro-chemical researches on various Objects, particularly the metallic bodies from the alkalis, an earths, and on some Combinations of Hydrogen.

Attempted to reduce  $\text{BeO}$  in platinum tube by potassium vapor without certain result. On fusing  $\text{BeO}$  in clay crucible with iron filings and potassium obtained a semi-malleable mass.

Phil. Trans., London, 100, 59.

Ann. der Phys. (Gilbert), 32, 395.

Ann. d. chim., (1) 75, 150.

Phil. Mag., 32, 152, 203.

- 1811; 1. Gay-Lussac, L. J., and Thenard, L. J. Recherches Physico-chimique.

Made a fluoride of beryllium by precipitating  $\text{HKF}_2$  with beryllium oxide dissolved in hydrochloric acid.

Ann. d. chim., (1) 78, 275.

- 1811; 2. John, J. F. Ueber einige unbekannte Verbindungen der Chromsaure mit verschiedenen Basen.

Dissolved basic carbonate in chromic acid, but could not crystallize any salt.

- 1812; 1. Stromeyer, F. Du memoire sur la reduction de la terre silicée, opérée par le moyen du charbon et du fer.

Claimed that he reduced magnesium and beryllium with great success by mixing the oxides with carbon, iron and linseed oil to a paste and melting in closed crucible, obtaining alloys with iron. Stromeyer was mistaken.

Ann. d. chim., (1) 81, 257.

- 1815; 1. Berzelius, J. J. Versuch durch Anwendung der Elektro-chemische Theorie und der chemischen Proportion Lehre Analyse der Beryllerde.

Prepared crystals for the first time of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ , which he considered an acid salt. By dissolving one and two equivalents of beryllium carbonate in this salt, he obtained on evaporation gummy masses containing the ratios  $2\text{BeO} \cdot \text{SO}_3$  and  $3\text{BeO} \cdot \text{SO}_3$  respectively. The first of these he considered the normal sulphate and the second a basic salt. On diluting the last with water he obtained a white precipitate to which he assigned the ratio  $6\text{BeO} \cdot \text{SO}_3$ . He also determined the atomic weight of beryllium from  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  and analyzed an impure chloride.

J. für Chem. (Schweigger), 15, 296.

- 1823; 1. Berzelius, J. J. Untersuchungen über die Flussspathesäure und deren merkwürdigsten Verbindungen.

Vet. Akad. Handl. (Stockholm), 1823, 302.

Ann. der Phys. (Pogg), 1, 22, 196.

Annals of Phil. (Thomson), 24, 330.

Made and described  $\text{BeF}_2$ . Dissolved  $\text{BeO}$  in  $\text{HF}$ . Obtained an easily soluble substance which dries to a gummy mass and which loses  $\text{H}_2\text{O}$  at  $100^\circ$ , becoming milk white and foamy. Loses part of its  $\text{HF}$  on ignition. Yields double salts with alkalies of which the potassium salt is very insoluble. Obtained a beryllium fluosilicate by action of fluosilicic acid.

- 1823; 2. Du Menil. Analyse des Sibirischen hellbläulichen Berylls (Aquamarine).  
J. für Chem. (Schweigger), 39, 487.  
Details method of analysis.
- 1825; 1. Berzelius, J. J. Ueber die Schwefelsalze.  
Kongl. Vet. Acad. Handl., 1825, 253; 275, 288, 311.  
Ann. d. Phys. (Pogg), 6, 453; 7, 23, 144, 273.  
Was not able to produce a sulphide of Be in solution.
- 1826; 1. Berzelius, J. J. Ueber die Bestimmung der relativen Anzahl von einfachen Atomen in chemischen Verbindungen.  
Ann. d. Phys. (Pogg), 8, 187.  
Valueless data on atomic weight, as he used a very basic sulphate. Gives oxides as  $\text{Be}_2\text{O}_3$ .
- 1826; 2. Berzelius, J. J. Ueber die Schwefelsalze.  
Kongl. Vet. Acad. Handl., 1826, part 1, 53.  
Ann. d. Phys. (Pogg), 8, 270.  
Thought he made a double sulphide of tungsten and beryllium by precipitating the double sulphide of potassium and tungsten with a beryllium salt. No formula or details.
- 1827; 1. Rose, H. Ueber die Verbindungen des Phosphors mit den Wasserstoffe und den Metallen.  
Ann. d. Phys. (Pogg), 9, 39.  
Berzelius Jsh., 8, 174.  
Ann. des Mines, (2) 3, 146.  
Made  $\text{BeCl}_2$  anhydrous for the first time. Passed chlorine over a heated mixture of the oxide and carbon and sublimed the product. Made beryllium phosphite by precipitating  $\text{BeCl}_2$  with a saturated solution of  $\text{PCl}_5$  in  $\text{NH}_4\text{OH}$ .
- 1828; 1. Rose, H. Ueber die unter Phosphorichsäuren Salze.  
Ann. der Phys. (Pogg), 12, 86.  
By saturating the acid with beryllium hydroxide obtained only a non-crystallizable gummy mass.

- 1828; 2. Wöhler, F. Ueber das Beryllium und Yttrium.

Ann. d. Phys. (Pogg), 13, 577.

Berzelius Jsb., 9, 96.

Mag. für Pharm., 26, 257.

Ann. des Mines, (2) 5, 133.

Ann. chim. phys., (2) 39, 77.

Reduced sublimed  $\text{BeCl}_2$  with potassium in platinum crucible and for the first time obtained metallic beryllium as a dark grey powder. Gives following properties, not all of which are sustained by later investigators: Burns in air and oxygen to  $\text{BeO}$  when heated on platinum. Dissolves in concentrated  $\text{H}_2\text{SO}_4$ , yielding  $\text{SO}_2$ . Dissolves in dilute  $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$  and  $\text{KOH}$ , giving off hydrogen. Dissolves in dilute  $\text{HNO}_3$  giving off nitric oxide. Not affected by  $\text{NH}_4\text{OH}$ . Burns in chlorine and bromine to  $\text{BeCl}_2$  and  $\text{BeBr}_2$ , both easily volatile and soluble with evolution of much heat. Burns in iodine gas and sublimes as  $\text{BeI}_2$  with properties similar to  $\text{BeCl}_2$  and  $\text{BeBr}_2$ .  $\text{BeS}$ , made by heating in sulphur vapor is a grey infusible mass difficultly soluble in  $\text{H}_2\text{O}$  which yields  $\text{H}_2\text{S}$  with acids.

$\text{BeSe}$ , made by heating in melted  $\text{Se}$  is fusible, but difficultly soluble.  $\text{BeTe}$ , a grey powder. Made beryllium phosphide by heating with phosphorous and beryllium arsenide by fusing with arsenic.

- 1828; 3. Bussy. Préparation du glucinium. Read at Acad. Roy. de Médic, Aug. 16, 1828.

J. chim. médicale, 4, 453.

J. für Chem. (Schweigger), 54, 241.

Berzelius Jsb., 9, 97.

J. de pharm., 1828, 486.

Polyt. J. (Dingler), 29, 466.

Prepared beryllium almost simultaneously with Wöhler and by the same method. Obtained an impure product, but did not study its properties extensively.

- 1828; 4. v. Bonsdorff, P. A. Beiträge sur Beantwortung der Frage ob Chlor, Jod und mehrere andere Metallöide,



sauern und basenbilden Körper wie der Sauestoffe sind.

Kongl. Vet. Acad. Handl., 1828, 174.

Ann. d. Phys. (Pogg), 17, 136.

Made a double chloride of mercury and beryllium in rhombic prisms, but gives no analysis or formula.

- 1831; 1. Berthemot. Beitrage sur Geschichte der Bromüre.  
Archiv. der Pharm., 37, 332.

J. de pharm., 26, 649.

Made bromide by dissolving BeO in HBr, but could not crystallize.

- 1831; 2. Becquerel, A. C. Considerations générales sur les Decomposition électro-chimique et la Reduction de l'oxide de fer, de la zircon et de la magnésie, a l'aide de forces électrique peu énergiques.

Ann. chim. et phys., 48, 350.

Pharm. Centrbl., 1832, 527.

Thought he reduced by the current BeCl<sub>2</sub>, which was impure with iron, but could not reduce pure BeCl<sub>2</sub>.

- 1831; 3. Berzelius, J. J. Ueber das Vanadin und seine Eigenschaften.

Ann. der Phys. (Pogg), 22, 58.

Obtained a yellow, neutral, difficultly soluble, powdered beryllium vanadate.

- 1832; 1. v. Kobell, Fr. Vermuthung über die Zusammensetzung der Beryllerde.

J. für Chem. (Schweigger), 64, 191.

J. prakt. Chem., 1, 92.

Claims that while CaCO<sub>3</sub> will precipitate the sesquioxides in the cold, it will not throw down manganese, zinc, iron or beryllium, but that beryllium is thrown out when the solution is heated near to boiling. Therefore, beryllium is bivalent.

- 1833; 1. Trommsdorff, J. B. Ueber die Valeriansaure und ihre Verbindungen Valeriansaure Beryllerde.  
Ann. der Chem. (Liebig), 6, 194.  
Ann. der Phys. (Pogg), 29, 159.  
Pharm. Centrbl., 1832, 310.  
Beryllium valerianate, made by dissolving carbonate in acid, dries to a sweet, gummy mass, unchangeable in air. (See Lacombe, 1902).
- 1833; 2. Berzelius, J. J. Untersuchung über die Eigenschaften des Tellurs.  
Kongl. Vet. Acad. Handl., 1833.  
Ann. der Phys. (Pogg), 32, 594, 607.  
Neutral beryllium tellurates and tellurites were precipitated by potassium tellurate or tellurite as white voluminous flakes.
- 1834; 1. Balard, A. G. Ueber Verbindungen des Broms mit Sauerstoff.  
J. prakt. Chem., 4, 165.  
Pharm. Centrbl., 1835, 349.  
Bibl. Univ., 1834, 372.  
Claims that bromine water partly dissolves BeO and that light has an apparent influence on the reaction.
- 1834; 2. Berzelius, J. J. Ueber die Destillations products der Traubensäure.  
Kongl. Vet. Acad. Handl., 1834.  
Ann. der Phys. (Pogg), 36, 17.  
Pharm. Centrbl., 1836, 41.
1837. 1. Heller, J. F. Rhodizonsäure, eine neue Oxidationsstufe des Kohlenstoffes und die Krokonsäure.  
J. prakt. Chem., 12, 227, 237.  
Pharm. Centrbl., 1837, 828, 833.  
Berzelius Jsb., 18, 521.  
Beryllium rhodonate,  $\text{Be}(\text{H}_2\text{C}_3\text{O}_6)$ , is a brown powder and was made by boiling an alcoholic solution of the acid with beryllium acetate. Beryllium krokonate,  $\text{Be}(\text{HC}_5\text{O}_4)$ , formed in yellow crystals was made same as preceding.

- 1838; 1. Biot, J. B. Des combinaisons fluides formés par l'acide tartrique, la glucine et l'eau.

Comptes. rend., 6, 158.

Used a tartrate of beryllium made by Berthier and found specific rotary power 100 millimeters to be +41.134 to +43.992, largest of any tartrate tried (see 1899; 13).

- 1840; 1. Gmelin, L. New Methode die Beryllerde von der Thonerde zu trennen.

Ann. der Phys. (Pogg), 50, 175-181.

Pharm. Centrbl., 2, 427.

Berzelius Jsb., 21, 141.

Ann. der Chem., 36, 207.

Ann. des mines, (4) 2, 70.

Chem. Gaz., 1, 9.

Separates iron, beryllium and aluminum as follows: The nearly neutral HCl solution is precipitated by cold KOH and digested in excess until the separated Fe-(OH)<sub>3</sub> has a clear brown color. The fluid is then diluted with water and boiled fifteen minutes. All beryllium separates out carrying some iron. Aluminum is determined in filtrate. Beryllium precipitate is ignited, dissolved and retreated to remove iron.

- 1840; 2. Schaffgotsch, F. Beitrage zur Kenntniss der Beryllerde.

Ann. der Phys. (Pogg), 50, 183-188.

Pharm. Centrbl., 2, 438.

Berzelius Jsb., 21, 95, 127, 141.

Ann. der Chem., 36, 206.

Ann. des mines, (4) 2, 170.

J. prakt. Chem., (1) 20, 376.

Phil. Mag., (3) 21, 284.

Chem. Gaz., 1, 9.

Analyzed the hydroxides and gives them with very doubtful amounts of H<sub>2</sub>O. The carbonate precipitated from ammonium carbonate solution and dried at 100° gave 47.53 per cent. BeO, 17.57 per cent. CO<sub>2</sub>, 34.90

per cent.  $\text{H}_2\text{O}$  (by dif.). Shows some relations of  $\text{Be}(\text{OH})_2$  to KOH as Gmelin (1840; 1) and may have priority. KOH must be neither too strong nor too weak. Says precipitate when well washed with  $\text{H}_2\text{O}$  is again soluble in KOH.

- 1840, 3. Scheerer, T. Untersuchung des Allanit, Orthit, Cerin und Gadolinit.

Ann. der Phys. (Pogg), 51, 472.

Was unable to obtain good results by method of Gmelin and of Schaffgotsch.

- 1842; 1. Rose, H. Die Zusammensetzung der Beryllerde.

Berichte der Akad. der Wis. (Berlin), 1842, 138-141.

J. prakt. Chem., 27, 120.

Berzelius Jsb., 22, 102.

Preliminary announcement and discussion of the results of Awdejew which were obtained under his direction.

- 1842; 2. Awdejew, v. Ueber das Beryllium und dessen Verbindungen.

Ann. der Phys. (Pogg), 56, 100-124.

Centrbl., 13, 627.

Berzelius Jsb., 23, 112 and 185.

Ann. d. Chem. (Liebig), 44, 269.

Ann. de chim. et phys., (3) 7, 155-173.

Phil. Mag., (3) 21, 284.

Berg u. Hut. Ztg., 1, 830.

Chem. Gaz., 1, 9.

An extended and valuable research. Found the conditions for the preparation of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ , purified it and correctly described its composition. Was the first to determine the atomic weight with even approximate accuracy. Determined atomic weight by analysis of sulphate. Was unsuccessful with chloride on account of its decomposition by water. Discusses the question of the valency of Be and came to the conclusion that it was a diad mainly from a study of the double salts of beryllium and potassium. Made the double fluoride

$2\text{KF} \cdot \text{BeF}_2$ . Gave the symbol  $\text{BeCl}_2$  to the chloride and thought he made  $\text{BeCl}_2 + 4\text{H}_2\text{O}$  by evaporation in vacuo which is undoubtedly a mistake.

- 1842; 3. Scheerer Th. Erste Fortsetzung der Untersuchungen über Gadolinit, Allanit und damit verwandte Mineralien.

Ann. der Phys. (Pogg), 56, 479.

J. prakt. Chem., 27, 76 and 80.

Centrbl., 1843, 208.

Berzelius Jsb., 23, 293.

Chem. Gaz., 1, 177.

Arch de pharm., 29, 214.

Read at Stockholm, July 15, 1842.

Separation of beryllium from iron. Uses ammonium sulphide to separate the small amount of iron dissolved by ammonium carbonate. First to propose this separation. Did not obtain good results by Schaffgotsch method of separation.

- 1843; 1. Rose, H. Ueber die Ytterde.

Ber. der Akad. der Wiss. Berlin, 1843, 143.

Ann. der Phys. (Pogg), 56, 105.

Separates beryllium from yttrium by volatility of the chloride on treating heated oxides mixed with carbon and with chlorine gas. The residue had to be dissolved in acid precipitated by ammonia and three times ignited with carbon and chlorine to remove all the volatile chlorides, but these chlorides contained no yttrium.

- 1843; 2. Berthier, P. Sur quelques séparations opérées au moyen de l'acide sulfureux en des sulfites alcaline.

Ann. de chim. et de phys., (3) 7, 74.

Ann. der Chem. (Liebig), 46, 182.

J. prakt. Chem., (1), 29, 68.

Centrbl., 1843, 378.

Separates beryllium from aluminum, cerium and yttrium after removal of most of the aluminum, as alum, by means of ammonium sulphite and boiling until no

more  $\text{SO}_2$  comes off. Aluminum, cerium and yttrium are precipitated, but beryllium remains dissolved.

- 1843; 3. Damour, A. Nouvelles analyses sur le cymophane de Haddam.

Ann. de chim. et de phys., (3) 7, 173.

Centrbl., 1843, 783.

Discusses the formulas  $\text{BeO}$  and  $\text{Be}_2\text{O}_3$  as applied to cymophane from basis of Awdejew's work.

- 1844; 1. Böttinger, Heinrich. Ueber die von Berthier vorge-schlagene Anwendung der schwefligen Säure in der chemischen Analyse.

Ann. der Chem. (Liebig), 51, 397.

Attempted to make quantitative separation of beryllium and aluminum by Berthier's method with sulphurous acid, but invariably found beryllium present with his aluminum.

- 1845; 1. Riess, P. Ueber das elektrische Leitungsvermögen einiger stoffe.

Ann. der Phys. (Pogg), 64, 53.

- 1847; 1. Peroz, J. Note sur les pyrophosphates doubles.

Ann. de chim. et de phys., (3) 20, 326.

Simply states that he made compounds of the alkaline pyrophosphates with beryllium pyrophosphate. No details.

- 1848; 1. Playfair, Lyon andn Joule, J. P. Researches on Atomic Volume and Specific Gravity.

J. Chem. Soc. (London), 3, 93.

Discussion of relation of atomic volume to specific gravity. No new results.

- 1848; 2. Rose, Heinrich. Ueber das Specifische Gewichte der Thonerde, der Beryllerde, der Magnesia und des Eisenoxyds.

Ber. der. Akad. d. Wiss. (Berlin), 1848, 165-170.

Centrbl., 1848, 485.

Ann. der Phys. (Pogg), 74, 433.

Jsb. Chem., 1, 398.

J. prakt. Chem., 44, 226.

l'Inst. (Paris), 1848, 368.

Ann. der. Chem. u. Pharm. (Liebig), 68, 167.

Beryllium oxide made by heating the basic carbonate over an alcohol lamp showed specific gravity=3.083-3.09. By heating to very high temperatures in porcelain oven became six-sided crystals and specific gravity=3.021. By heat hydroxide precipitated by ammonia, specific gravity=3.096. Same to much higher temperature, specific gravity=3.027.

- 1848; 3. Rose, Heinrich. Ueber die Anwendung des Salmiak in der Analytische Chemie.

Ber. der. Akad. der Wiss. (Berlin), 1848, 202.

Centrbl., (1848) 19, 602.

J. prakt. Chem., 45, 116.

Ann. der. Phys. (Pogg), 83, 145.

Beryllium carbonate, oxide, etc., are only partly decomposed by heating with ammonium chloride.

- 1850; 1. Rivot, L. E. De l'emploi de l'hydrogene dans les analyses des substances minerales.

Ann. de chim. et de phys., (3) 30, 188.

Ann. Chem. u. Pharm. (Liebig), 78, 212.

J. prakt. Chem., 51, 338.

Centrbl., 1850, 908.

Jsb. Chem., 3, 599.

Chem. Gaz., 9, 76.

Separates iron oxide from beryllium oxide by igniting in hydrogen and dissolving out iron in dilute nitric acid (1-30) or determines per cent. of iron from loss on ignition in hydrogen.

- 1851; 1. Ebelmen, J. J. Recherches sur la cristallization par voie sèche.

Comptes rend., 33, 526.

Ann. Chem. (Liebig), 80, 211.

Crystallized beryllium oxide from an alkali silicate and obtained six-sided prisms with a density of 3.058. Hard enough to scratch glass, insoluble in acids, although

slightly in hot concentrated  $\text{H}_2\text{SO}_4$ . Easily soluble in  $\text{HKSO}_4$ . Claims perfectly isomorphous with crystals of  $\text{Al}_2\text{O}_3$ .

- 1851; 2. Ebelmen, J. J. Ueber die Krystallization auf trockenem Wege.

J. prakt. Chem., 55, 342.

Centrbl., 1851, 529, 899.

Jsb. Chem., 4, 15.

l'Inst. (Paris), 1851, 179, 369.

Same as 1851; 1, but separately transmitted by author.

- 1851; 3. Ebelmen, J. J. Sur une nouvelle methode pour obtenir des combinaisons cristallisées par la voie seche (sur la cymophane).

Ann. de chim. et de phys., (3) 33, 40.

Made cymophane artificially by fusing together  $\text{Al}_2\text{O}_3$ ,  $\text{BeO}$  and  $\text{B}_2\text{O}_3$ .

- 1853; 1. Fremy, E. Recherches sur les sulfures décomposables par l'eau; suivé de considerations générales sur la production des eaux sulfureuses et siliceuses.

Comptes rend., 36, 178.

Centrbl., 1853, 113.

Says sulphide of beryllium was the only sulphide he could not make by passing  $\text{CS}_2$  over hot base.

- 1853; 2. Müller, H. Mineralanalysen.

J. prakt. Chem., 58, 181.

Several analyses of beryl with methods used but embodying nothing new.

- 1854; 1. Weeren, Julius. Einige Beiträge zur Kenntniss der Beryllerde.

Ann. der Phys. (Pogg), 92, 91-128.

J. prakt. Chem., 62, 301.

Ann. Chem. (Liebig), 92, 262.

Centrbl., 1854, 705.

Jsb. Chem., 7, 336 and 728.

Chem. Gaz., 12, 408.

Amer. J. Sci., (2), 18, 414.

An extended and careful research on beryllium. De-



terminated atomic weight by ratio  $\text{BeO} : \text{SO}_3$  in carefully purified sulphate. Compared different methods of preparation. Considered methods by use of  $(\text{NH}_4)_2\text{CO}_3$  and by  $\text{NH}_4\text{Cl}$  best. Gives special precautions for latter.

Studied  $\text{Be}(\text{OH})_2$  critically and gives properties. Studied carbonates and found no definite composition, but varying proportions of carbonate and hydroxide according to treatment. Gives formulas for some of these as obtained, all showing a high ratio of base to acid.

Found the sulphate lost one third of its water of crystallization at  $35^\circ\text{C}$ .

- 1854; 2. Debray, Henri. Du glucyrum et de ses composés. Academic Dissertation, Paris.

Comptes rend., 38, 784.

Centrbl., 1854, 448.

Jsb. Chem., 7, 336.

J. prakt. Chem., 62, 180.

Ann. Chim., (Liebig), 92, 261.

Chem. Gaz., 12, 204; 13, 386.

Chemist, 1, 558.

Arch. ph. nat., 26, 181.

l'Institute, (Paris), 1854, 142.

Arch. der Pharm., 142, 44.

First announcement to French academy of results much more fully described in 1855; 1.

- 1855; 1. Debray, Henri. Du glucinum et de ses composés. Academic Dissertation, Paris, 1855.

Ann de. chim. et de phys., (3), 44, 1-41.

Centrbl., 1855, 549.

Jsb. Chem., 8, 356.

Chem. Gaz., 13, 386.

J. Chem. Soc., (London), 8, 242.

Extended research. Made beryllium by reduction of chloride by sodium as a white metal, specific gravity 2.1, and describes properties. Could not make the sulphide

as Wohler did. Made and described  $\text{BeO}$ ,  $\text{BeCl}_2$ ,  $\text{BeI}_2$ ,  $\text{BeF}_2 \cdot \text{KF}$ ,  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ ,  $\text{K}_2\text{SO}_4 \cdot \text{BeSO}_4 \cdot 2\text{H}_2\text{O}$ . Made rather indefinite basic carbonates, obtaining quantities equivalent to  $2\text{Be}(\text{OH})_2 \cdot \text{BeCO}_3 \cdot 3\text{H}_2\text{O}$  as one of his products. Also made double carbonates with ammonium and potassium. Could not make crystalline oxalates but easily prepared the double oxalates,  $\text{BeC}_2\text{O}_4$ ,  $\text{K}_2\text{C}_2\text{O}_4$ , and  $\text{BeC}_2\text{O}_4 \cdot (\text{NH}_4)_2\text{C}_2\text{O}_4$ . Studied the properties of the hydrate,  $(\text{Be}(\text{OH})_2)$ . Decomposed his beryl by fusing with lime. Gives a new method of separation from aluminum by the action of zinc on mixed sulphates, hydrogen being evolved, and the aluminum precipitated as a basic sulphate. Favored bivalency of beryllium.

- 1855; 2. Rose, Heinrich. Ueber des Verhalten der verschiedenen Basen gegen Lösungen amoniacalischer Salze und namentlich gegen die Lösung von chlorammonium. Ber. Akad. d. Wiss. (Berlin), 1855, 334.  
Centrbl., 1855, 612.

Found that beryllium oxide could decompose solutions of ammonium chloride but lost this property when very strongly heated. This property belongs to bases  $\text{RO}$  and not  $\text{R}_2\text{O}_3$ .

- 1855; 3. Rose, Heinrich. Ueber die atomische Zusammensetzung der Beryllerde.  
Ber. Akad. d. Wiss. (Berlin), 1855, 581.  
Ann. der Phys. (Pogg), 96, 445.  
J. prakt. Chem., 64, 182.  
Centrbl., 1855, 730, 733.  
Jsb. Chem., 8, 361.  
l'Insntitute (Paris), 1856, 111.  
Chem. Gaz., 13, 466.

Discussion of previous work, (1848; 2) and concludes that from atomic volume considerations, constitution of oxide must be  $\text{R}_2\text{O}_3$  in spite of results with ammonium chloride (1855; 4).

- 1857; 1. Lewy, B. Recherches sur la formation et la composition des émeraudes.  
Comptes rend., 45, 877.  
Concluded color of emerald was due to organic matter and not to chromium.
- 1858; 1. Ordway, John M. Examination of soluble basic sesqui salts.  
Amer. J. of Sci., (2) 26, 197.  
J. prakt. Chem., 76, 22.  
Jsb. Chem., 11, 114.  
Discusses the formation of the nitrate but finds it very difficult to crystallize. Made basic compounds by drying solution of nitrate.
- 1858; 2. Lea, M. Carey. On picric acid and some of its salts.  
Amer. J. of Sci., (2) 26, 382.  
Centrbl., 1859, 121.  
Carbonate of beryllium dissolves readily in hot aqueous picric acid and by evaporation yields golden yellow crystalline crusts.
- 1858; 3. Deville, St. Claire and Caron, H. Sur un nouveau mode de production à l'état cristallisé d'une certain nombre d'espèces chimiques et minéralogiques.  
Comptes rend., 46, 765.  
Chemist, (3) 5, 514.  
Fused equal equivalents of fluorides of aluminum and beryllium under high heat in boric acid.
- 1859; 1. Hofmeister. Über die Trennung der Beryllerde von der Alaunerde, nebst der Analyse zweier Beryll.  
J. prakt. Chem., 76, 1.  
Rep. chem. pure, 1, 301.  
Jsb. Chem., 12, 675.  
Archiv. der Pharm., 101, 177.  
Used ammonium carbonate method and proposed a number of fractional precipitations to remove all aluminum.

- 1859; 2. Ordway, John M. Some facts respecting the nitrates.  
Amer. Jour. Sci., (2) 57, 18.  
J. prakt. Chem., 76, 22.

Solid nitrate of beryllium melts as low as  $140^{\circ}$  F., and may be cooled as low as  $85^{\circ}$  F., before it begins to solidify. Boiled as low as  $285^{\circ}$  F., continuing to boil and remaining clear to  $320^{\circ}$  F., giving off acid all the time. The highly basic residue did not solidify on cooling to  $61^{\circ}$  F., on adding strong nitric acid solidified and temperature rose to  $142^{\circ}$  F. Dilution with a "basic salt" has therefore same effect as dilution with  $H_2O$ .

- 1859; 3. Scheffer, G. Beitrage zur Kenntniss der Beryllerde.  
Ann. Chem. (Liebig), 109, 144.  
J. prakt. Chem., 77, 79.  
N. arch. ph. nat., 5, 180.  
Ann. chim. et phys., (3) 56, 112.  
Rep. chim. pur., 1, 317.  
Archiv. der Pharm., 33, 144.  
Jsb. Chem., 12, 139.  
Le Moniteur scientifique, 2, 862.  
Phil. Mag., (4) 18, 455.

Scheffer claims to have decomposed his beryl by heating in a lead dish at  $100-200^{\circ}$  with  $CaF_2$  and concentrated  $H_2SO_4$ . Made an acid phosphate,  $BeHPO_4 \cdot 3H_2O$  which on drying yielded  $BeHPO_4 \cdot H_2O$  and a gummy phosphate,  $5BeO \cdot 2P_2O_5 + 8H_2O$  which on dilution with water yielded a white precipitate,  $2BeO \cdot P_2O_5 + 5H_2O$ . These results are interesting as they are quite analogous to the basic sulphate action while in reality they are acid compounds if phosphoric acid is tribasic. Claimed to make a nitrate by evaporating  $BeO$  and  $HNO_3$  to dryness at  $120^{\circ}-150^{\circ}$ . Claimed it then lost no  $H_2O$  or  $N_2O_5$  (which is not true of any nitrate of beryllium. Obtained first class results by Debray's method of separation with zinc. By precipitating basic beryllium nitrate with  $Na_4P_2O_7$  obtained a pulverulent precipitate, the analysis of which would

yield the formula,  $\text{Be}_2\text{P}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ . Made a triple salt,  $\text{BeNa}_2(\text{NH}_4)_2(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$  by adding  $\text{NH}_4\text{Cl}$  before precipitating with sodium phosphate.

- 1860; 1. Cahours, Aug. Recherches sur les radicaux organo-metallique, "Glucinium ethyl."

Ann. chim. et phys., (3) 58, 22.

Made beryllium ethyl by action of metallic beryllium on  $\text{C}_2\text{H}_5\text{I}$  in sealed tube. Appeared analogous to aluminum ethyl, but did not have enough to study.

- 1861; 1. Frankland, E. On organo metallic bodies.

J. Chem. Soc. (London), 13, 181, 194.

Discusses briefly conclusions of Cahours (1860; 1) on beryllium ethyl.

- 1862; 1. Parkman, Theodore. On the carbonates of Alumina, Glucina and the sesquioxides of Iron, Chromium and Uranium.

Amer. J. of Sci., (2) 34, 326.

Centrl., 1863, 465, 468.

Chem. News, 7, 122.

By precipitating  $\text{BeSO}_4$  with  $\text{Na}_2\text{CO}_3$  in slight excess he obtained a basic carbonate containing the approximate ratio of  $3\text{BeO}:\text{CO}_2$ .

- 1863; 1. Joy, Charles A. On Glucinum and its Compounds.

Amer. J. of Sci., (2) 36, 83.

Chem. News, 8, 183, 197.

J. prakt. Chem., 92, 232.

Jsh. Chem., 16, 676.

Centrl., 1864, 1119.

Bull. soc. chim., (2) 2, 351.

An extended and excellent study of the methods of decomposing beryl and separating beryllium from aluminum including an extended bibliography of the subject and of the minerals containing beryllium.

Tried the following methods of decomposing beryl:

1. By passing chlorine over calcined beryl, oil and lamp-black in hot porcelain tube. Chloride of iron, aluminum and beryllium volatilized together.

2. By treating beryl with concentrated HF and  $\text{H}_2\text{SO}_4$ . Claimed to succeed if beryl was very finely pulverized.
  3. By digesting seven parts beryl, 13 parts  $\text{CaF}_2$  in 18 parts  $\text{H}_2\text{SO}_4$ . Decomposed but large amount of calcium compounds proved a great disadvantage.
  4. By fusing beryl with three parts of KF and digesting with  $\text{H}_2\text{SO}_4$ . Fine method except for cost of KF.  $\text{SiF}_4$  is driven off at low heat.
  5. By  $\text{NH}_4\text{F}$ , ditto.
  6. By digesting in  $\text{H}_2\text{SO}_4$  and fusing with potassium ferrocyanide and salt. Complete failure.
  7. By fusing with  $\text{CaF}_2$ . Attacked crucible badly and large amount of calcium compounds caused complications.
  8. By fusing two parts beryl with one part CaO in Hessian crucible. Attacked crucible, but claimed decided advantages if suitable crucible could be found.
  9. By fusing with litharge. Not so good as with  $\text{K}_2\text{CO}_3$ .
  10. By fusing with  $\text{MnO}_2$ . Decomposed but no advantage.
  11. By fusing a mixture of two parts  $\text{Na}_2\text{CO}_3$  and three parts  $\text{K}_2\text{CO}_3$ . Worked well, but preferred the following.
  12. By fusing one part beryl with two parts  $\text{K}_2\text{CO}_3$ . Preferred this method to any of the others. Fused mass decomposed with  $\text{H}_2\text{SO}_4$ , evaporated to get rid of silica, crystallized out alum, etc.
- Joy also tried the following for separating beryllium from aluminum:
1. By  $\text{NH}_4\text{Cl}$ . Precipitated by  $\text{NH}_4\text{OH}$  and digested in concentrated solution of  $\text{NH}_4\text{Cl}$  with addition of evaporated water. Iron and aluminum remain insoluble and beryllium goes into solution. Tedious, but accurate.
  2. By carbonate of ammonium. Some aluminum also goes into solution, although it does not when alone.

3. By caustic potash. Mixed solution in HCl is precipitated with KOH which is gradually added in excess until precipitate dissolves, then diluted with 10 volumes of water and boiled. Beryllium precipitates partially and fairly free from aluminum and iron, but much loss of beryllium.
  4. By sulphurous acid. Did not succeed as some beryllium was always thrown down with the basic sulphite of aluminum.
  5. By  $\text{BaCO}_3$ . Both precipitated.
  6. By  $\text{Na}_2\text{S}_2\text{O}_3$ . Both precipitated.
  7. By decomposing the nitrates heated to 200 to 250. Both acted the same.
  8. By acetate of soda. Beryllium, aluminum and iron act the same.
  9. By fusion with KOH. Act alike.
  10. By ammonium formate. Act alike.
  11. By decomposition of sulphates. Act alike.
  12. By formation of alum. Considers this best.
- 1864; 1. Wöhler, F., and Rose, G. Sur la nature colorante des émeraudes.  
Comptes rend., 58, 1180.  
Chem. News, 10, 22.  
Deny coloring matter of emerald due to organic matter and heated to prove. Imitate color in glass by a small amount of chromium.
- 1864; 2. Gibbs, Wolcott. On the quantitative separation of cerium from yttrium, aluminum, glucinum, manganese, iron and uranium.  
Amer. Jour. of Sci., (2) 37, 354.  
J. prakt. Chem., 94, 121.  
Chem. News, 10, 195.  
Ztschr. f. Chem., 1865, 15.  
Separates beryllium from cerium group by its solubility in saturated sodium sulphate; from yttrium group by oxalate of ammonia.

- 1864; 3. Gibbs, Wolcott. On the employment of fluohydrate of fluoride of potassium in analysis.

Amer. J. of Sci., (2) 37, 356.

Centrbl., 1864, 990.

Jsb. Chem., 17, 684.

J. prakt. Chem., 94, 121.

Ztschr. f. Chem., 1865, 16.

Chem. News, 10, 37 and 39.

Bull. soc. chim., (2) 4, 359.

States that fusing crude BeO with HF. KF and treating the fused mass with boiling water and slight amount of HF and recrystallization is the best known (1864) method of producing a chemically pure salt of beryllium. Under these conditions the aluminum is separated as the very insoluble  $\text{AlF}_3 \cdot 3\text{KF}$ . Also states that NaF precipitates the aluminum probably quantitatively from a mixture of the fluorides of aluminum and beryllium.

- 1864; 4. Gibbs, Wolcott. Beitrage zur Chemie aus dem Laboratorium der Lawrence Scientific School.

Ztschr. anal. Chem., 3, 397, 399.

Same as 1864, 2 and 3.

- 1865; 1. Delafontaine, Marc. Metals in Gadolinite.

Chem. News, 11, 159.

Archiv. d. sci. phys. and nat. Geneva, 97, 101.

- 1866; 1. Cooke, J. P. On Danalite, a New Mineral Species from the Granite of Rockland, Mass.

Amer. J. Sci., (2) 42; 78.

Ztschr. anal. Chem., 6, 226.

Gives method of analysis and discusses method of St. Clair Deville (Annales., 38). Says it is one of the most accurate in analytical chemistry. Separates beryllium from iron by reducing iron in platinum tube in a current of hydrogen and then volatilizing in a current of HCl. Aluminum and beryllium not effected. See 1850, Rivot.



- 1866; 2. Hermes, O. Beiträge zur Kenntniss der Schwefelcyanverbindungen.

J. prakt. Chem., 97, 475.

Centrl., 1867, 112.

Made  $\text{Be}(\text{CvS})_2$  by action of  $\text{H}(\text{CvS})$  on carbonate. Soluble in alcohol. Salt poorly defined and doubtful.

- 1867; 1. Debray, H. Report to the Société chimique de Paris on beryllium on exhibition at the Paris Exposition.

Bull. soc. chim., (2) 7, 495.

Simple statement (no details) that Debray reported on metallic beryllium exhibited at the Paris exposition, which was manufactured by M. Ménier by heating with sodium, a mixture of  $\text{BeCl}_2$  and the double fluorides of beryllium and potassium in a crucible of pure aluminium.

- 1869; 1. Klatzo, Georg. Die Constitution der Beryllerde.

Academic Dissertation, Dorpat.

Ztschr. f. Chem., 12, 129.

Centrl., 1869, 832.

Bull. soc. chim., (2) 12, 131.

N. arch. phys. nat., 34, 354.

Joh. Chem., 12, 203; 13, 256.

J. prakt. Chem., 106, 227-244.

Trds. for Phys. og. Chem., 8, 167.

Ztschr. anal. Chem., 8, 202 and 523.

Chem. News, 19, 227.

J. Frank. Inst., 89, 260.

An extended article full of erroneous work as shown by Marignac and others. Studied sulphates and claimed to make a new sulphate,  $\text{BeSO}_4 \cdot 7\text{H}_2\text{O}$ .

By saturating the basic carbonate with  $\text{CO}_2$  in water and evaporating in an atmosphere of  $\text{CO}_2$ , he claimed to obtain crystals of  $\text{BeCO}_3 \cdot 4\text{H}_2\text{O}$  which formed double salts with alkaline carbonates.

By precipitating ammonium carbonate solution with alcohol, claimed to make the compound  $3\text{BeCO}_3 \cdot \text{BeO}$ .

$\text{H}_2\text{O} + 3(\text{NH}_4)_2\text{CO}_3$ . Made a basic carbonate of formula similar to that obtained by Debray.

Determined the atomic weight by ignition of sulphate.

Studied the chloride and fluoride.

- 1869; 2. Thalen, Rob. Mémoire sur la détermination des longueurs d'onde des raies métalliques.

Nova Acta Reg. Soc. Sc. Upsal. (3) vol. 6.

Ann. chim. et phys., (4) 18, 228.

Found the wave length of the bright rays of the Beryllium spectra to be 4572 in the blue and 4488.5 in the indigo.

- 1870; 1. Thomsen, Julius. Ueber Berylliumplatinchlorid.

Berichte, 1870, 827.

Centrbl., 1870, 690.

Jsb. Chem., 1870, 318.

J. Chem. Soc. (London), 24, 202.

Bull. soc. chim., (2) 15, 50.

Ztschr. f. Chem., 14, 46.

Chem. News, 22, 263.

J. Applied Chem., 5, 185.

Made  $\text{BePtCl}_6 \cdot 8\text{H}_2\text{O}$ .

- 1871; 1. Thomsen, J. Die Wärmeentwicklung der Neutralization.

Ann. der Phys. (Pogg), 143, 497.

Berichte, 4 (1871), 586.

Bull. soc. chim., (2) 16, 63.

Jsb. Chem., 1871, 102.

Determined among many others, the heat of neutralization of  $\text{Be}(\text{OH})_2$  with sulphuric and hydrochloric acid.

Found  $\text{Be}(\text{OH})_2 + \text{H}_2\text{SO}_4 + \text{Aq} = 16100$ ,  $\text{Be}(\text{OH})_2 + 2\text{HCl} + \text{Aq} = 13640$ .

- 1871; 2. Toczyński, F. Ueber die Platincyanide und Tartrate des Beryllium.

Ztschr. f. Chem., 15, 275.

Inaugural Dissertation, Dorpat, 1871.

Bull. soc. chim., (2) 16, 254.

Centrbl., 1871, 564; 1872, 517.

Jsb. Chem., 1871, 286, 359.

Pharm. Ztschr. f. Russl., 11, 166, 204.

J. Chem. Soc. (Lon.), 24, 1013.

Chem. News, 24, 158.

Made green ferrocyanide of Beryllium by precipitating barium salt with  $\text{BeSO}_4$ . Made ferricyanide by oxidizing ferrocyanide with Cl, olive green. Could not separate the sulphocyanate and nitroprusside.

Made  $\text{BePtCy}_4 + 4\text{H}_2\text{O}$  by precipitating barium salt in crystals, changing on heating through gold, yellow, orange red.

Made  $\text{BeMg}_2\text{Pt}_3\text{Cy}_{12} \cdot 16\text{H}_2\text{O}$  by crystallizing the two cyanides together.

Made several very complicated and basic double tartrates to which he gave formulas.

1872; 1. Topsøe, Haldor. Krystallographische-chemische Untersuchungen.

Stizber. d. k. Akad. Wiss. Wein, 66, II, 5.

Jsb. Chem., 1872, 163.

N. arch. sci. phys. nat., 45, (1872), 76.

$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ , tetragonal  $a:c = 1:0.9461$ . Observed form (011).(110) uniaxial, negative, specific gravity 1.725.

$\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$ , at  $100^\circ$  loses two molecules  $\text{H}_2\text{O}$ , specific gravity 2.029. Rhombohedral,  $a:b:c = 1:0.9602:0.90275$ . Observed forms (011).(101).(021).(111).(001).

Also made isomorphous mixtures of the sulphate and selenate and studied crystals of same.

1873; 1. Cahours, A. Recherches sur de nouveaux dérivés du propyle.

Comptes rend., 76, 1383.

Centrbl., 1873, 482.

Jsb. Chem., 1873, 520.

Berichte, 6, 821.

J. Chem. Soc. (London), 26, 871.

J. Russ. Phys. and Chem. Soc., 5, 274.

Made beryllium propyl by acting on mercury propyl at

130-135° in sealed tube. Beryllium propyl was distilled in atmosphere of  $\text{CO}_2$  to a colorless liquid boiling at 244-246°. Fumes in air and is spontaneously combustible. Thick oil at 17°. Decomposed by  $\text{H}_2\text{O}$ . Also confirms earlier experiments 1860; 1 on beryllium ethyl and prepared same in like manner to above with boiling point 185-188° and properties similar.

- 1873; 2. Marignac, C. de. *Notices chimiques et cristallographiques sur quelques sels de glucine et des métaux de la céri-te.*

N. arch. d. sci. phys. nat., 46, 193.

Ann. chim. et phys., (4) 30, 45-69.

Jsb. Chem., 1873, 259.

Chem. News, 28, 45.

J. Chem. Soc. (London), 27, 24.

J. Russ. Phys. and Chem. Soc., 5, II, 303.

Confirms Awdejew (1842; 2)  $2\text{KF} \cdot \text{BeF}_2$  and made also  $\text{KF} \cdot \text{BeF}_2$ ,  $2\text{NaF} \cdot \text{BeF}_2$ ,  $\text{NaF} \cdot \text{BeF}_2$ ,  $2\text{NH}_4\text{F} \cdot \text{BeF}_2$ . Confirms  $\text{K}_2\text{SO}_4 \cdot \text{BeSO}_4 \cdot 2\text{H}_2\text{O}$ . Concluded that beryllium is not isomorphous with Al or Mg group. Gives forms of crystals and finds many differences from Klatzo, (1869; 1).

- 1873; 3. Williams, C. Grenville. *Researches on Emeralds and Beryls. I. On the coloring matter of the emerald,*

Phil. Mag., (4) 46, 314.

Proc. Roy. Soc., 21, 409.

Fused emeralds and beryls in oxyhydrogen blow-pipe and made artificial emeralds and beryls by simply fusing constituents together. Concluded coloring matter to be due to chromic oxide.

- 1873; 4. Thomsen, Julius. *Untersuchung über die Wärmtönung beim Auflösen verschiedener fester flüssiger und luftformiger Körper in Wasser.*

Berichte, 6, 712.

By dissolving one molecule  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  in 400 molecules of water, found heat of solution = + 1100.

- 1873; 5. Welkow, A. Beryllium Platinchloride.

Berichte, 6, 1288.

Centrbl., 1874, 50.

Bull. soc. chim., (2) 21, 273.

Amer. Chem., 4, 390.

Jsb. Chem., 1873, 258.

J. Chem. Soc. (London), 27, 229.

Chem. News, 29, 51.

Made  $\text{BePtCl}_6 \cdot 8\text{H}_2\text{O}$ , tetragonal, dark yellow crystals  
see Thomsen, 1870; 1.

- 1873; 6. Töpsoc, Haldor. Tabelle über die specifischen Gewichte, Moleculargewichte, und Molecularvolumen verschiedene Salze.

Centrbl., 1873, 76.

Contains summary of his work 1872; 1 and also calculates molecular volume from data then given.

- 1873; 7. Atterberg, Albert. Undersökningar öfver Metallen Berylliums Föreningar.

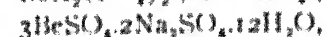
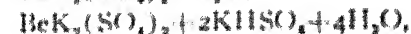
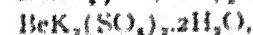
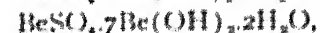
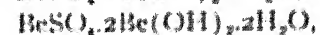
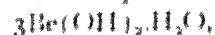
Kongl. Svenska Vetenskaps-Akademiens.

Handlingar, 12, 1-38.

Chem. Centrbl., 1874, 330.

Berichte, 7, 472.

Atterberg especially calls attention to the tendency of beryllium to form substances of a highly basic nature and claims to have made the following compounds:



# BIBLIOGRAPHY OF BERYLLIUM

$\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$ ,  
 $\text{BeSO}_3 \cdot \text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ ,  
 $\text{BeSeO}_3 \cdot \text{H}_2\text{O}$ ,  
 $2(\text{BeSeO}_3 \cdot \text{H}_2\text{O}) \cdot \text{Be}(\text{OH})_2$ ,  
 $2\text{BeSeO}_3 \cdot \text{Be}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$ ,  
 $\text{BeSeO}_3 \cdot \text{Be}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ,  
 $\text{BeSeO}_3 \cdot \text{Be}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ ,  
 $\text{BeCrO}_4 \cdot 13\text{Be}(\text{OH})_2 + 10\text{H}_2\text{O}$ ,  
 $\text{BeMoO}_4 \cdot \text{Be}(\text{OH})_2 + 2\text{H}_2\text{O}$ ,  
 $\text{BeMoO}_4 \cdot \text{MoO}_3 \cdot \text{H}_2\text{O}$ ,  
 $2\text{BeCl}_2 \cdot 3\text{HgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  
 $\text{BeC}_4\text{H}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$  (succinate),  
 $\text{BeC}_4\text{H}_4\text{O}_4 \cdot \text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ ,  
 $\text{BeCl}_2 \cdot 4\text{H}_2\text{O}$ ,  
 $\text{BeCl}_2 \cdot 3\text{Be}(\text{OH})_2$ ,  
 $\text{BeCl}_2 \cdot 12\text{Be}(\text{OH})_2 + 10\text{H}_2\text{O}$ ,  
 $\text{BeCl}_2 \cdot \text{SnCl}_4 \cdot 8\text{H}_2\text{O}$ ,  
 $\text{BeCl}_2 \cdot \text{AuCl}_3$ ,  
 $\text{Be}(\text{ClO}_4)_2 \cdot 4\text{H}_2\text{O}$ ,  
 $\text{Be}_3(\text{IO}_4)_2 + 11\text{H}_2\text{O} + 13\text{H}_2\text{O}$ ,  
 $\text{Be}_3(\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$ ,  
 $\text{BeC}_2\text{O}_4 \cdot \text{Be}(\text{OH})_2 \cdot \text{H}_2\text{O}$ ,  
 $\text{BeC}_2\text{O}_4 \cdot 6\text{Be}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$ ,  
 $\text{BeC}_4\text{H}_4\text{O}_6 \cdot 3\text{H}_2\text{O}$ ,

Many of which, in fact, have no existence as definite compounds.

- 1873; 8. Atterberg, A. Faits pour servir a l'histoire der glucinium.

Bull. soc. chim., 19, 497.

Jsb. Chem., 1873, 257.

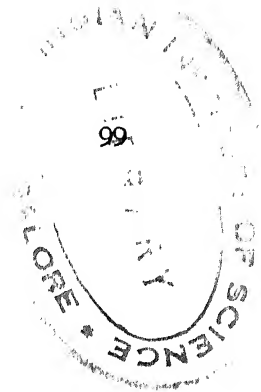
Chem. Centrbl., 1873, 530.

J. Chem. Soc. (London), 26, 1003.

J. Russ. Phys. and Chem. Soc., 5, II, 303.

Separately transmitted, but contains nothing not in 1873; 7, except  $\text{BeSO}_4 \cdot 5\text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ .

- 1873; 9. Topsøe, H and Christiansen, C. Recherches optiques sur quelques series de substances isomorphes.



Ann. chim. et phys., (5) 1, 5.

Complete from Vidensky, Selsk., 1873, 9, 625.

Ann. der Phys. (Pogg), Erganz-Bd., 6, 499.

Chem. Centrbl., 1874, 258.

$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ , optically negative.

Tetragonal  $a:c=1:0.9461$ .

Mean values indices of refraction.

C = 1.4374	C = 1.4691
$\epsilon$ D = 1.4395	$\omega$ D = 1.4720
F = 1.4450	F = 1.4779

$\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$ , rhombohedral.  $a:b:c=1:0.9602:0.9027$ .

Mean indices.

	$\mu_a$	$\mu_b$	$\mu_c$
C	1.4992	1.4973	1.4639
D	1.5027	1.5007	1.4664
F	1.5101	1.5084	1.4725

1873; 10. Holst, N. O. Bidrag till Kännedomen om Platinas Cyanföreningar.

Ars-skrift. Univ. Lund., 10, II, No. 6.

Bull. soc. chim., (2) 22, 349.

Chem. Centrbl., 1874, 786.

Berichte, 8, 125.

Jsb. Chem., 1875, 238.

Made the salt  $\text{BePtBr}_2\text{Cy}_4$  in crystals.

1874; 1. Atterberg, Albert. Sur les combinaisons du glucinium.

Bull. soc. chim., (2) 21, 157.

Berichte, 7, 472.

J. Chem. Soc. (London), 27, 658.

Ztschr. anal. Chem., 13, 316.

J. Russ. Chem. and Phys. Soc., 6, II, 84.

Separately transmitted, but contains nothing not in 1873; 7.

1874; 2. Thomsen, J. Die Neutralizationswärme der oxyde des Lanthans, Ceriums, Didyms, Yttriums and Erbium.

Berichte, 7, 33.

Uses his previously obtained figures for  $\text{Be}(\text{OH})_2$  in discussion.

1874; 3. Welkow, A. Beryllium-Palladiumchlorid.

Berichte, 7, 38.

Chem. Centrbl., 1874, 50, 245.

Jsb. Chem., 1874, 254.

J. Chem. Soc. (London), 27, 443.

Amer. Chem., 4, 469.

Chem. News, 29, 155.

Gaz. chim. ital., 4, 278.

Bull. soc. chim., 2, (21) 273.

Made  $\text{BePdCl}_6 + 8\text{H}_2\text{O}$ , dark red brown crystals, loses all of its water at  $130^\circ$ . Isomorphous with  $\text{BePdCl}_6 + 8\text{H}_2\text{O}$ .

- 1874; 4. Thomsen, J. Beryllium-Platinchlorid.

Berichte, 7, 75.

Chem. Centrbl., 1874, 245.

Note to the effect that he had priority over Welkow and that Marignac had corrected his  $9\text{H}_2\text{O}$  to  $8\text{H}_2\text{O}$  which he found correct.

- 1874; 5. Welkow, A. Aluminum-Platinchlorid.

Berichte, 7, 306.

Bull. soc. chim., (2) 22, 153.

Gaz. chim. ital., 4, 302.

Chem. Centrbl., 1874, 292.

States that his comparisons with the beryllium salt show no crystallographic resemblance and does not lead to placing Be in Al group.

- 1874; 6. Welkow, A. Beryllium-Palladiumchlorür.

Berichte, 7, 803.

Chem. Centrbl., 1874, 476.

Jsb. Chem., 1874, 254.

J. Chem. Soc. (London), 27, 1065.

Amer. Chemist, 5, 264.

Bull. soc. chim., (2), 22, 499.

Gaz. chim. ital., 5, 61.

By heating conc. solution of  $\text{BePdCl}_6 \cdot 8\text{H}_2\text{O}$  chlorine is evolved and  $\text{BePdCl}_4 \cdot 6\text{H}_2\text{O}$  left in soluble, brown tabular crystals. Also obtained a double iodide of Be and Sb, and Be and Bi which were so unstable, he could not assign a satisfactory formula, but found no re-



semblance to corresponding Al compound. Could not make double chlorides with alkali metals.

- 1875; 1. Bunsen, R. W. Spectral Analytische Untersuchung. Ann. d. Phys. (Pogg), 155, 230, 366.  
Ztschr. anal. Chem., 15, 92.

Short reference to spectra of Be.

- 1875; 2. Nilson, L. F. Zur Frage über die Valenz der selten Erdmetalle.  
Berichte, 8, 655.  
Chem. Centrbl., 1875, 449.

Claims to have made the following salts,  $5\text{BeO} \cdot 2\text{SeO}_2 + 10\text{H}_2\text{O}$ ,  $\text{BeSeO}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{BeSeO}_3\text{H}_2\text{SeO}_3$ ,  $\text{BeSeO}_3 \cdot 2\text{H}_2\text{SeO}_3$ , which, he says, indicate the BeO rather than  $\text{Be}_2\text{O}_3$  formula.

- 1875; 3. Nilson, L. F. Recherches sur les sélénites.  
Nova Acta reg. Soc. Sci. Upsala 1875, transmitted by Cleve to Bull. soc. chim., (2), 23, 355.  
Same as 1875; 2, but separately transmitted and contains besides those enumerated there,  
 $5\text{BeO} \cdot 8\text{SeO}_2 \cdot 5\text{H}_2\text{O}$ ,  
 $3\text{BeO} \cdot 7\text{SeO}_2 \cdot 5\text{H}_2\text{O}$ .

- 1875; 4. Atterberg, A. Några Ytterligare bidrag till Kännedomen om Beryllium föresingarna.  
Ofvrvsgt. Köngl. Vet. Akad. Forhand, 1875, No. 7, 32.  
Bull. soc. chim. (2), 24, 358.  
Chem. Centrbl, 1876, 35.  
Berichte, 9, 856.  
Jour. Chem. Soc. (London), 30, 382.  
Gaz. chim. ital., 6, 159.

Communicated through M. Cleve, prepared  $\text{BeCl}_2 \cdot 2((\text{C}_2\text{H}_5)_2\text{O})$ . Claims that his previously given formula,  $3\text{BeCl}_2 \cdot 2\text{Be}(\text{OH})_2$ , was incorrect and should be  $\text{BeO} \cdot \text{HCl}$ .

Also made  $\text{BeHPO}_4 \cdot 3\text{H}_2\text{O}$ ,  $\text{Be}_3(\text{PO}_4)_2 \cdot 6$  or  $7 \text{H}_2\text{O}$ ,  
 $\text{Be}_3(\text{AsO}_4)_2 \cdot 6\text{H}_2\text{O}$ ,  
 $\text{BeHAsO}_4 \cdot 2\text{H}_2\text{O}$ .

- 1876; 1. Nilson, L. F. Zur Frage über die Valenz der seltenen Erdmetalle.  
Berichte, 9, 1056, 1145.  
Jsb. Chem., 1876, 292.  
Bull. soc. chim. (2), 27, 206.  
J. Russ. Phys. and Chem Soc., 9, II, 98.  
Amer. Chemist, 7, 242.  
J. prakt. Chem., 15, 177.  
Discusses the work of others on  $\text{BePtCl}_6 \cdot 8\text{H}_2\text{O}$ , and makes  $\text{BePtCl}_4 \cdot 5\text{H}_2\text{O}$ . Again places Be in divalent metals.
- 1876; 2. Nilson, L. F. Untersuchung über Chlorosalze und Doppel nitrite des Platins. (Beryllium plato and di-platonitrite).  
Nov. Acta. Soc. Sci. Upsala (3) vol. extra, (1877), number 15. Ofvst. Akad. Handl. (Stockholm), 33, number 23.  
Berichte, 9, 1722.  
J. prakt. Chem. (2), 16, 264.  
Chem. Centrbl., 1878, 211.  
Chem. News, 34, 270; 37, 31.  
Jsb. Chem., 1876, 295, 1877, 310.  
Bull. soc. chim. (2), 27, 210, 245.  
Treated  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  with barium plato nitrite, filtered and evaporated in vacuum. Obtained  $\text{Be}(2\text{NO}_2 \cdot \text{Pt})_2 \cdot \text{O} \cdot 9\text{H}_2\text{O}$  (diplatonitrite), but could not make the platonitrite. Makes  $\text{BePtCl}_4 + 5\text{H}_2\text{O}$ .
- 1876; 3. Reynolds, J. Emerson. On Glucinum, its atomic weight and specific heat. (Read April 10, 1876).  
Phil. Mag., (5) 3, 38-42.  
Bull. soc. chim., (2) 28, 161.  
Chem. Centrbl., 1877, 210.  
Chem. News, 35, 119.  
J. Chem. Soc. (London), 31, 579.  
Berichte, 9, 1806.  
J. Russ. Phys., and Chem. Soc., 9, II, 244.  
Reduced  $\text{BeCl}_2$ , made from beryl, by Na in platinum crucible below fusion and determined specific heat com-

pared to silver in special calorimeter. Found specific heat = 0.642 at 100°, at. heat 5.91. Concluded at. wt. therefore to be 9.2.

- 1877; 1. Williams, C. Grenville. Researches on Emeralds and Beryls. II.

Chem. News, 35, 257.

Analysis and study of separation of Be and Al. Nothing especially new.

- 1877; 2. Cossa and Pecile. Einwirkung von Fluormagnesium auf des sulphate des Aluminums und Berylliums.

Berichte, 10, 1099.

Formed fluoride of both metals.

- 1878; 1. Smith, Edgar F. Beryllum borate.

Proc. Amer. Chem. Soc., 2, 114.

Found that if  $\text{BeCl}_2$  was precipitated with excess of borax and precipitate washed with hot water, only  $\text{Be}(\text{OH})_2$  was left.

- 1878; 2. Nilson, L. F. and Pettersson, Otto. Ueber die specifische Wärme des Berylliums.

Berichte, 11, 381.

Tids Krift, 17, 109.

Short report to German Chem. Soc. of 1878; 3 and 1878; 4.

- 1878; 3. Nilson, L. F. and Pettersson, Otto. Ueber Darstellung und Valenz des Berylliums.

Ann. der Phys. (Wied), 4, 554-585.

Nova Acta. Soc. Sci. Upsala, 10, (1879), number 9, Chem. Centrbl., 1878, 275, 610.

Jsb. Chem., 1878, 70, 241.

Amer. Jour. Sci. (3), 15, 386; 16, 384.

Chem. News., 37, 225.

Very complete article. Historical review, preparation of (87 per cent.) metal by decomposition of chloride by sodium. Fused metal under salt in closed iron crucible. Properties of metal and list of "all well characterized" compounds made up to that time. List contains many of very doubtful composition and omits some that prob-

ably do exist. Concluded Be to be trivalent. Specific gravity  $\text{Be}=1.64$ , specific heat at  $6^\circ=0.2471$ . Could not make sulphide.

- 1878; 4. Nilson, L. F. and Pettersson, Otto. Sur les propriétés physiques et sur la chaleur spécifique de glucinium.

Comptes rend., 83, 823.

Ann. die chim. et de phys. (5), 14, 426.

Bull. soc. chim. (2), 31, 442.

Separately presented by M. Berthelot. Complete in Annales. Same as 1878; 3.

- 1878; 5. Meyer, Lothar. Ueber das Atomgewicht des Berylliums.

Berichte, 11, 576.

Chem. Centrbl., 1878, 370.

Chem. News, 38, 9.

J. Chem. Soc. (London), 34, 557.

J. Russ. Phys. and Chem. Soc., 11, II, 49.

Discusses 1878; 3 and 4 and questions conclusion that Be is trivalent.

- 1878; 6. Brauner, B. Ueber das Atomgewicht des Berylliums  
Berichte, 11, 872.

Chem. Centrbl, 1878, 467.

Jsb. Chem., 1878, 70.

Chem. News., 38, 59.

J. Chem. Soc. (London), 34, 704.

J. Russ. Phys. and Chem. Soc., 11, II, 49.

Discusses N. and P. (1878; 3), work on specific heat and predicts that if determined at higher temperature and density of  $\text{BeCl}_2$  be found, Be will be found to be divalent.

- 1878; 7. Nilson, L. F. Om jodhaltiga derivat of platonitrit, (Beryllium platojodonitrite).

Ofvsgrt, Akad. För. Stockholm, 35, number 3, 51.

Nova Acta Soc. Sci. Upsala, 10, (1879), number 16.

Berichte, 11, 884.

J. prakt. Chem., 21, 172, (complete).

Bull. soc. chim., (2), 31, 361.

Chem. News., 38, 49.

J. Chem. Soc. (London), 34, 706.

Chem. Centrbl., 1880, 261.

Jsb. Chem., 1878, 312.

J. Russ. Chem. Soc., 11, 11, 305.

Made  $\text{BePtI}_2(\text{NO}_2)_2 + 6\text{H}_2\text{O}$ .

- 1878; 8. Nilson, L. R. and Pettersson, Otto. Ueber das Atomgewicht des Berylliums, (Erwiderung an Lothar Meyer).

Berichte, 11, 906.

J. Russ. Phys. and Chem. Soc., 11, 11, 49.

Discussion of 1876; 3 and 1878; 5.

- 1878; 9. Rössler, C. Ueber die Nachweisung des Berylliums.

Ztschr. anal. Chem., 17, 148.

Chem. Centrbl., 1878, 600.

Jsb. Chem., 1878, 1059.

Chem. tech. Rep., 1878, 422.

J. Chem. Soc. (London), 34, 606.

Bull. soc. chim. (2), 32, 365.

J. Russ. Phys. and Chem. Soc., 11, 83.

By adding an excess of ammonium phosphate to a beryllium salt, dissolving the precipitate in HCl, adding  $\text{NH}_4\text{OH}$  to neutral reaction, avoiding excess, and heating to boiling, precipitate becomes crystalline and settles quickly. Na phosphate not applicable. Serves to separate from small amounts of Al if citric acid is present. Larger amounts of Al must first be removed by heating to  $180^\circ$  in sealed tube with excess of saturated solution of  $\text{K}_2\text{SO}_4$ . His phosphate was analogous to the similar magnesium compound, but varied somewhat in composition so he did not assign formula.

- 1878; 10. Lockyer, V. N. Researches in spectrum analysis in connection with the spectrum of the sun.

Proc. Roy. Soc. (London), 27, 279.

Includes Be in table of elements probably present in sun.

- 1878; 11. Sorret, J. L. Recherches sur l'absorption des rayons ultra violets.

Arch des sci. phys. et nat. de Geneve, (2), 63, 108.  
1878 and (3), 4, 290, 1880.

Solutions of  $\text{BeCl}_2$  give no absorption bands but partially absorb the ultra violet light, the absorption increasing with the refrangability.

Ultra violet light from an induction spark gives a faint blue fluorescence to a solution of beryllium chloride.

- 1879; 1. Carnalley, T. Influence of atomic weight on physical properties of compounds. (Melting points of  $\text{BeCl}_2$  and  $\text{BeBr}_2$ ).

Phil. Mag., (5), 8, 281.

Chem. News., 39, 281.

Chem. Centrbl., 1880, 339.

Jsb. Chem., 1879, 18.

J. Chem. Soc. (London), 37, 125.

Obtained melting point of  $\text{BeCl}_2$  and  $\text{BeBr}_2$ , between  $858-890^\circ$ , which are in reality several hundred degrees too high.

- 1879; 2. Mendeleef, D. La Loi Périodique des Elémentes chimiques.

Moniteur scientifique, 39, 691.

Chem. News., 40, 303.

Place of beryllium in system.

- 1880; 1. Carnalley, T. and Carleton, Williams, W. The melting and boiling points of certain inorganic solvents.

J. Chem. Soc. (London), 37, 125.

Apparently again determined the melting points of  $\text{BeCl}_2$  and  $\text{BeBr}_2$  as between  $585-617^\circ$ , but on next page repeats his old figures of  $858-890^\circ$ , both of which are much too high.

- 1880; 2. Vincent, Camille. Note sur les réactions produits par la di-méthylamine aqueuse sur les dissolutions métalliques.

Bull. soc. chim., 33, 157.

Chem. Centrbl., 1880, 278.

Zeit. anal. Chem., 17, 479.

Dimethyl amine precipitates beryllium from solutions of its salts as a white precipitate insoluble in excess, (also Fe," F<sub>2</sub>''' and Zr). Says like precipitate from Al salts is soluble in excess. See also Renz, 1903.

- 1880; 3. Humpidge, T. S. Atomic weight of beryllium.

Chem. News., 42, 261.

Chem. Centrbl., 1881, 36.

Jsb. Chem., 1880, 290.

Berichte, 13, 2412.

Agrees with Nilson and Petersson that Be is trivalent.

- 1880; 4. Reynolds, J. Emerson. Atomic weight of beryllium, note on.

Chem. News., 42, 273.

Chem. Centrbl., 1881, 68.

Jsb. Chem., 1880, 289.

Berichte, 13, 2412.

- 1880; 5. Ciamician, G. L. Über des Spectrum des Berylliums Sitzber, Akad. Wein (2), 82, 425.

Monatshefte für Chemie, 1, 662.

Ztschr. anal. Chem., 20, 411.

Spark spectra between beryllium electrodes is homologous with spectra of C. B and Mg. Obtained only a spectra of second order, a three-fold line 2 c: 509.7; 508.8; 508., in green and an intense violet line 3 c, 401.5.

- 1880; 6. Nilson, L. F., and Pettersson, Otto. Om berylliums atomwigt och väsendtliga egenskaper (atomic weight and essential properties).

Ofers. af. K. Sven. Vet. Akad. Förh., 1880, No. 6, page 33.

Berichte, 13, 1451-59.

Chem. Centrbl., 1880, 612.

Jsb. Chem., 1880; 4, 238.

Jour. Chem. Soc. (London), 38, 850.

Chem. News, 45, 13.

Jour. Russ. Phys. and Chem. Soc., 13, II, 273.

Ztschr. anal. Chem., 21, 483.

Determined atomic weight by ignition of hydrous sulphate. Sulphate made from sublimed chloride and crystallized three times from excess of  $\text{H}_2\text{SO}_4$ . Dried between blotting paper.

Made metal 94 per cent. pure and determined specific heat at  $300^\circ = 5056$ .

Long discussion favoring trivalency of beryllium.

- 1880; 7. Nilson, L. F., and Pettersson, Otto. On the Essential Properties and Chemical Characters of Beryllium.

Read before Royal Soc., Nov. 18, 1880.

Chem. News, 42, 297.

Berichte, 14, 259.

J. Chem. Soc. (London), 40, 511.

Separate presentation of 1880; 6.

- 1880; 8. Nilson, L. F. and Pettersson, Otto. Sur le poids atomique et les propriétés principales du glucinum.

Comptes rend., 91, 168.

J. Chem. Soc. (London), 38, 792.

Separate report to French Academy of 1880; 6, but not so complete as in Berichte, 13, 1451.

- 1880; 9. Nilson, L. F., and Pettersson, Otto. Om de sällsyn-  
ta jordarternas och deras sulfats molekylarvärme och-  
volym. (The molecular heat and molecular volume  
of the rare earths and their sulphates).

Of. af. K. Sv. Akad. Förh., 1880, No. 6, p. 45.

Berichte, 13, 1459.

Jsb. Chem., 1880, 291.

Found the following figures based on trivalency of Be:

$\text{Be}_2$ . Molecular weight, 75.3; specific gravity, 3.016; specific heat, 2471; molecular heat, 18.61

$\text{Be}_2(\text{SO}_4)_3$ . Molecular weight, 315.3; specific gravity, 2.443; specific heat, 0.1978.

$\text{Be}_2(\text{SO}_4)_3 + 12\text{H}_2\text{O}$ . Molecular weight, 531.3; specific gravity, 1.713

$\text{Be}_2\text{O}_3$  diamagnetic.



- 1880; 10. Nilson, L. F., and Pettersson, Otto. Sur les chaleur et le volume moléculaires des terres rare et de leur sulfates.

Comptes rend., 91, 232.

Separate report to the French Academy of 1880; 9.

- 1880; 11. Meyer, Lothar. Ueber das Atomgewicht des Beryllium.

Berichte, 13, 1780.

Bull. soc. chim., (2) 36, 152.

Chem. Centrbl., 1880, 1789.

Arch. der Pharm., 218, 68.

Chem. Ztg., 4, 752.

Chem. News, 46, 159.

J. Russ. Phys. and Chem. Soc., 13, II, 273.

J. Chem. Soc. (London), 40, 139.

Amer. Chem. J., 2, 360.

Discussion of results of Nilson and Pettersson and others and comes to the conclusion that Be is divalent.

- 1880; 12. Nilson, L. F. Zur Frage nach dem Atomgewicht des Berylliums:

Berichte, 13, 2035.

J. Chem. Soc. (London), 40, 140.

Chem. Centrbl., 1881, 36.

Amer. Chem. J., 2, 433.

Reply to 1880; 11.

- 1881; 1. Brauner, Bohuslav. Ueber das Atomgewichte des Berylliums.

Berichte, 14, 53.

Chem. Centrbl., 1881, 298.

Jsb. Chem., 1881, 4.

Phil. Mag., (5) 11, 65.

J. Chem. Soc., 40, 224.

Chem. Ztg., 5, 79.

J. Russ. Phys. and Chem. Soc., 14, II, 63.

Excellent discussion of the probable valency of Beryllium and favors divalency.

- 1881; 2. Reinsch, H. Ueber die Erkennung und Unterscheidung der Kiesel-Thon, und Beryllerde, der Borsäure der Alkalien und einiger Metalle durch das Mikroskop. Berichte, 14, 2325.  
Chem. Centrbl., 1882, 56.  
Jsb. Chem., 1881, 1183.  
Bull. soc. chim., (2) 37, 525.  
Chemisches Ind., 4, 428.  
Arch. der. pharm., 220, 68.

Says that the sulphate forms very characteristic crystals under the microscope which enables it to be identified at once.

- 1881; 3. Classen, Alex. Elektrolytische Bestimmung und Trennung. Berichte, 14, 2782.  
Chem. Centrbl., 1882, 233.  
Jsb. Chem., 1882, 1152.  
Ding. Poly. J., 242, 440.  
Bull. soc. chim., (2) 37, 526.  
Ztschr. anal. Chem., 22, 440.

Separates Fe and Al from Be by electrolysis in ammonium oxalate solution. Iron reduced. Aluminum precipitated by use of stronger current, as hydroxide by ammonium carbonate produced and beryllium left in solution.

- 1881; 4. Crookes, W. On Discontinuous Phosphorescent Spectra in High Vacuo. Proc. Roy. Soc., 32, 206.  
Chem. News, 43, 237.  
Annales chim. et phys., (5) 23, 555 (complete).  
Comptes rend., 92, 1281.  
Jsb. Chem., 1881, 130.

Carefully prepared BeO gave a fluorescence of a beautiful blue, but no spectral rays. Under conditions given it shows only a concentration of light in the blue.

- 1882; 1. Blake, James. Atomic weight of beryllium as determined by its physiological actions.

Chem. News, 45, 111.

Jsb. Chem., 1882, 15.

J. Chem. Soc. (London), 42, 701.

Found that physiological action of sulphate injected into the blood was analogous to members of aluminum family, from which he concludes that beryllium is trivalent.

- 1882; 2. v. Bemmelen, J. M. Die Hydrate des Beryll oxyds.

J. prakt. Chem., (2) 26, 227-246.

Bull. soc. chim., (2) 39, 514.

Chem. Centrbl., 1883, 36.

Jsb. Chem., 1882, 275.

Berichte, 15, 2902.

Chem. News, 46, 291.

J. Chem. Soc. (London), 44, 291.

Rec. trav. chim. de Pays Bas., 1, 271.

J. Russ. Phys. and Chem. Soc., 15, II, 453.

A long study of the hydroxides of beryllium. Distinguishes two hydroxides, 1st. Alpha, made by boiling KOH solution, and 2nd. Beta, made by precipitating salts with ammonia. Only the first has definite composition.

- 1882; 3. de Boisbaudran, Lecoq. Séparation du gallium.

Comptes rend., 94, 1439.

Jsb. Chem., 1882, 1295.

Separated from beryllium by precipitating gallium by potassium ferrocyanide in acid solution.

- 1883; 1. Wallroth, K. A. Action du sel de phosphore sur divers oxydes.

Bull. soc. chim., 39, 316.

Chem. Centrbl., 1883, 290.

Obtained  $\text{BeNaPO}_4$  by fusing  $\text{BeO}$  in sodium metaphosphate. Insoluble hexagonal plates.

- 1883; 2. Philipp, Jul. Ueber basisches Beryllium-Kalium Oxalate.  
Berichte, 16, 752.  
Jsb. Chem., 1883, 1045.  
Bull. soc. chim., (2) 40, 373.  
Mentions Debray's  $\text{BeC}_2\text{O}_4 \cdot 3\text{K}_2\text{C}_2\text{O}_4$  and  $\text{Be}(\text{C}_2\text{O}_4)_3$ .  
 $3(\text{NH}_4)_2\text{C}_2\text{O}_4$  and states that last salt is characteristic in its crystallization for beryllium and is valuable in purification. Made a new salt to which he gave the trivalent formula  $\text{Be}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{K}_2\text{C}_2\text{O}_4 \cdot \text{Be}_2(\text{OH})_6 + 5\text{H}_2\text{O}$ , by saturating acid potassium oxalate with  $\text{Be}(\text{OH})_2$ , evaporating and cooling in desiccator.
- 1883; 3. Donath, Ed. and Mayrhofer, J. Bemerkungen über Affinität und deren Beziehungen zu Atomvolum, Atomgewicht und specific Gewicht.  
Berichte, 16, 1590.  
Jsb. Chem., 1883, 26.  
Uses determinations of others on beryllium in his discussion.
- 1883; 4. Clarke, F. W. A recalculation of the Atomic Weights. (Glucinium).  
Chem. News, 48, 289. (From Constants of Nature).  
Chem. Ztg., 8, 21.  
A recalculation of all determinations of atomic weight of beryllium up to 1883 and discussion of same.
- 1883; 5. Hartly, W. N. On the Spectrum of Beryllium with observations relative to the position of the metal among the elements.  
J. Chem. Soc. (London), 43, 316.  
Chem. Centrbl., 1883, 380.  
Jsb. Chem., 1883, 246.  
Bull. soc. chim., (2) 41, 642.  
Chem. News, 47, 201.  
J. Amer. Chem. Soc., 5, 115.  
J. Russ. Phys. and Chem. Soc., 16, II, 63.  
Studies spectrum of beryllium and concludes that conclusion of Nilson and Pettersson is wrong as to tri-

valency of beryllium and claims that its spectra shows it to be the first member of a dyad series of which, in all probability, Ca, Ba, and Sr are homologues. Article contains fine chart of spectra of beryllium.

- 1883; 6. Haushofer, K. Beitrage zur mikroskopischen Analyse Sitzungsberichte 'd. Kön. Bayr. Akad. der Wiss., 1883, p. 436; 1884, p. 690.  
Ztschr. für Kryst., 11, 166; 13, 173.  
Berichte, 18, 238.  
Jsb. Chem., 1885, 1880.

Recommends beryllium platinum chloride, which is easily soluble in water as microscopic test for Be. Made by action of  $\text{PtCl}_4$  on beryllium salt and evaporation in desiccator. Tetragonal crystals.

- 1883; 7. Humpidge, T. S. On the Atomic Weight of Glucinum.  
Chem. News, 47, 181.  
Proc. Roy. Soc. (London), 35, 137.  
Trans. Roy. Soc. (London), 174, 601.  
Chem. Centrbl., 1883, 380.  
Jsb. Chem., 1883, 35.  
Chem. Ztg., 7, 648.  
Berichte, 16, 2494.

Determined specific heat as 4453 from a 94 per cent. metal made by action of Na on  $\text{BeCl}_2$ . Speaks of the possibility of electrolyzing double fluoride of K and Be, but says material is very impure from fluorine attacking containing vessel. Gives many properties of Be and  $\text{BeO}$  not consistent with those of later investigators. Main study was evidently on specific heat, which being obtained at low temperatures, lead him to the belief in trivalent beryllium.

- 1883; 8. Reynolds, J. Ernerson. Atomic Weight of Beryllium, Note on.  
Chem. News, 47, 251.  
Proc. Roy. Soc. (Lon.), 35, 248.  
Chem. Centrbl., 1883, 471.

- Jsb. Chem., 1883, 36.  
Jour. Chem. Soc. (Lon.), 46, 261.  
Berichte, 16, 2494.
- 1883; 9. Humpidge, T. S. Reply to a note by J. E. Reynolds on the Atomic Weight of Glucinum or Beryllium.  
Chem. News, 47, 297.  
Proc. Roy. Soc. (Lon.), 35, 358.  
Chem. Centrbl., 1883, 501.  
Jsb. Chem., 1883, 35.  
Chem. Ztg., 7, 873.  
Berichte, 16, 2659.
- 1883; 10. Reynolds, J. Emerson. Note in Regard to Humpidge's "Reply" on Beryllium.  
Chem. News, 48, 9.
- 1884; 1. Penfield, Sam'l L. On the occurrence of alkalies in Beryl.  
Amer. J. of Sci., (3) 28, 25.  
Found Na, Li and  $H_2O$  present, also Cs in two samples.  
Gives method of analysis used.
- 1884; 2. Lavroff, V. L'action du beryllium metalique sur le mercure-dimethyle, (Preliminary announcement of 1884; 3).  
Bull. soc. chim., (2) 41, 548.
- 1884; 3. Lavroff, V. Beryllium Methyl.  
J. Russ. Phys. and Chem. Soc., 16, 93.  
By the action of metallic beryllium on mercury methyl in sealed tubes at  $130^\circ$ , he obtained a white volatile crystalline substance, decomposed by water with evolution of light into methane and  $Be(OH)_2$ .
- 1884; 4. Brögger, W. C., and Flink, Gust. Ueber Krystalle von Beryllium und Vanadium.  
Ztschr. für Kryst., 9, 228-236.  
Berichte, 17, 849.  
Chem. Ztg., 8, 670.  
Bul. de la soc. franc. d. min., 7, 412.  
Bull. soc. chim., (2) 43, 561.  
J. Chem. Soc. (Lon.), 46, 1092.

Used the beryllium crystals made by Nilson and Pettersson by action of Na on  $\text{BeCl}_2$ .

System Hexagonal and holohedral.

Type I. Prismatic crystals.

$$\infty P : \infty P' \quad 59^\circ, 59\frac{1}{2}'.$$

$$\infty P' : \infty P'' \quad 60^\circ, 11\frac{1}{2}'.$$

$$\infty P : oP \quad 89^\circ, 55\frac{1}{2}'.$$

Type II. Tabular crystals.

$$P : P \quad 57^\circ, 31'.$$

$$P' : P' \quad 56^\circ, 20', (\text{poor})$$

$$P : \infty P \quad 28^\circ, 11'.$$

Axis relation

$$a:c = 1:1.5862.$$

Also examined crystals made by T. S. Humpidge and found them to belong to the holohedric division of Hexagonal System.

- 1884; 5. Hartley, W. N. The Atomic Weight of Beryllium, Remarks on.

Proc. Roy. Soc. (Lon.), **36**, 462.

Chem. News, **49**, 171.

Jsb. Chem., **1884**, 49.

J. Chem. Soc. (Lon.), **48**, 484.

Discussion of his previous work on Spectra of Beryllium and its position among the elements.

- 1884; 6. Genth, F. A. On Herderite.

Proc. Amer. Phil. Soc., **21**, 694.

Chem. News, **51**, 86.

Points out that  $\text{BeO}$  is slightly soluble in a boiling solution of  $\text{NH}_4\text{Cl}$ , and discusses methods of determining  $\text{BeO}$ .

- 1884; 7. Nilson, L. F., and Pettersson, Otto. Ueber die Dampfdichte des Chlorberylliums.

Berichte, **17**, 987.

Jsb. Chem., **1884**, 61.

Chem. Ztg., **8**, 669.

Bull. soc. chim., **44**, 32.

- Amer. J. Sci., (3) 28, 149.  
Tidskrift, 23, 310.  
Arch. der. Pharm., 222, 462.  
Amer. Chem. J., 6, 215.
- Found the density of  $\text{BeCl}_2$  at different points between  $490^\circ$  and  $812^\circ$ , overthrew all their previous ideas of the subject and proved the divalency of beryllium. Full details of preparation, apparatus and method used.
- 1884; 8. Nilson, L. F. and Pettersson, Otto. Determinations de la densité des vapeurs du chlorur de glucinium.  
Comptes rend., 98, 988.  
Chem. News, 49, 255.  
J. Chem. Soc. (Lon.), 46, 820.  
Chem. Centrbl., 1884, 452.  
Separately transmitted to French academy. Same as 1884, 7.
- 1884; 9. Carnalley, T. Applications of Melting and Boiling points to the classification of the Atomic Weights of Elements.  
Phil. Mag. (5), 18, 21.  
Uses same result of previous work, (1879; 1) in discussion.
- 1884; 10. Carnalley, T. Ueber die Schmelzpunkte von Chlor und Bromberyllium.  
Berichte, 17, 1357.  
J. Chem. Soc. (Lon.), 46, 962.  
Repeats with careful precaution his earlier work and defends his previous results (1879; 1), which are much too high.
- 1885; 1. Humpidge, T. S. On the Atomic Weight of Glucinium.  
Proc. Roy. Soc. (Lon.), 38, 188.  
Chem. News, 51, 121.  
Jsb. Chem., 1885, 32.  
J. Am. Chem. Soc., 7, 113.  
J. Chem. Soc. (Lon.), 48, 1184.  
Berichte, 18, 258.  
Advance report of 1886; 1.



- 1885; 2. Tammann, G. Ueber die Dampftensionen von Salzlosungen.

Ann. der. Phys. (Wied.), **24**, 554.

Mem. de l'academy imp. de St. Pets'bg. **35**, No. 9, 1887.

Ztschr. phys. Chem., **2**, 45.

Jsb. Chem., **1888**, 185.

Gives figures on the lowering of the vapor tension by beryllium sulphate in comparison with other sulphates. Shows its molecular weight to be represented by  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ . Gives results also for chloride, bromide and nitrate.

- 1885; 3. Nilson, L. F. and Pettersson, Otto. Ueber ein Neues mit exacter Temperature Bestimmung verbundenes Verfahren zur Feststellung der Dampfdichte flüchtiger Körper. Read at Kon. Ak. der. Wiss. Stockholm, Sept. 16, 1885.

Jr. prakt. Chem. (2), **33**, 1-17, (complete).

Ann. de chim. et de phys. (6), **9**, 554, (complete).

Chem. Centrbl., **1886**, 130.

Jsb. Chem., **1886**, 59.

J. Russ. Chem. and Phys. Soc., **18**, II, 92.

Prepared  $\text{BeCl}_2$  in platinum by action of dry  $\text{HCl}$  on  $\text{Be}$  and redetermined density between  $490^\circ$  and  $1520^\circ$  C. Obtained quite closely agreeing results above  $1000^\circ$ . Interesting description of apparatus used to prevent the chloride coming in contact with water or glass. Decided addition to previous work.

- 1886; 1. Humpidge, T. S. Atomic weight of beryllium.

Proc. Roy. Soc. (Lon.), **39**, 1.

Jsb. Chem., **1886**, 44.

J. Chem. Soc. (Lon.), **50**, 506.

Berichte, **19**, 202.

J. Russ. Phys. and Chem. Soc., **18**, II, 111.

Determined specific heat of  $\text{Be}$  on a specimen 99.2 per cent. pure at temperatures up to  $450^\circ$ . The curve representing relation between specific heat and tempera-

- ture reaches a maximum at  $400^{\circ}$  and remains practically constant between  $400^{\circ}$  and  $500^{\circ}$ . Figures obtained places Be with C. B. and Si, as accordant with law of Dulong and Petit at high temperature. Also determine density of  $\text{BeCl}_2$  and  $\text{BeBr}_2$ .  
Also made a double carbonate of evidently indefinite composition to which he gives the formula:  $2(\text{BeCO}_3 \cdot (\text{NH}_4)_2\text{CO}_3) \cdot \text{Be}(\text{OH})_2 + 2\text{H}_2\text{O}$ .
- 1886; 2. Grandeaun, H. De l'action du sulfate de potasse a temperature élevée sur les phosphates metalliques.  
Ann. de chim. et de phys. (6), 8, 212.  
Jsb. Chem., 1886, 358.  
Made  $\text{K}_2\text{Be}_2(\text{PO}_4)_2$  by fusing the sulphate and phosphates together. Specific gravity  $\text{BeO} = 3.18$ .
- 1886; 3. Strohecker, R. Beryll oxyd in diluvialen Thonen.  
J. prakt. Chem., (2) 33, 132.  
Jsb. Chem., 1886, 407.  
Chem. News, 53, 136; 54, 207.
- 1886; 4. Penfield, S. L. and Harper, D. N. Chemical composition of Herderite and Beryl.  
Am. J. Sci., (3) 32, 107.  
Chem. News, 54, 90.  
Berichte, 19, 797.  
Chem. industrie, 10, 366.  
Analysis and discussion of methods of separation of beryllium from aluminum.
- 1886; 5. Chabrie, C. Note préliminaire sur les fluosilicates d'aluminium et de glucinium.  
Bull. soc. chim., (2) 46, 284.  
Chem. Centrbl., 1886, 771.  
Jsb. Chem., 1886, 399.  
J. Chem. Soc., 50, 981.  
Berichte, 19, 871.
- 1886; 6. Cooke, J. P. On Danalite, a new Mineral Species from the Granite of Rockland, Mass.  
Amer. J. Sci. (2), 42, 78.  
Ztschr. and Chem. 6, 226.

Gives method of analysis and separated iron from beryllium by reducing the former in a current of hydrogen and volatilizing it in a current of hydrochloric acid gas.

- 1887; 1. Meyer, Lothar. Ueber die Einwirkung von Chlor kolenstoff auf Oxyde.

Berichte, 20, 681.

Jsb. Chem., 1887, 379.

Found he could make many metallic chlorides by passing  $\text{CCl}_4$  over oxides when heated, among them  $\text{BeCl}_2$ .

- 1887; 2. Ebel, Fr. Ueber antimonisaure Salze.

Berichte, 22, 3044.

J. Chem. Soc. (Lon.), 58, 216.

Made  $\text{BeSb}_2\text{O}_6 \cdot 6\text{H}_2\text{O}$  by dissolving  $\text{Na}_2\text{H}_2\text{Sb}_2\text{O}_7 \cdot 7\text{H}_2\text{O}$  in boiling water and adding a soluble beryllium salt.

- 1887; 3. Crookes, W. Radiant Matter Spectroscopy. Examination of the residual glow.

Proc. Roy Soc., 42, 111.

J. Chem. Soc. (Lon.), 52, 1066.

Examined  $\text{BeO}$  among other oxides. Found it to give a rich blue, but no residual glow.

- 1887; 4. Mallard, E. Sur quelques substances cristallisées préparées par Ebelmen.

Bul. de la soc franc. de min., 11, 305.

Ztschr. f. Kryst., 14, 605; 15, 650.

Ann. d. mines, 12, 427, 460.

Comptes rend., 105, 1260.

Jsb. Chem., 1887, 384.

J. Chem. Soc. (Lon.), 54, 349.

By fusing chromic oxide and  $\text{BeO}$  in presence of boric anhydride and calcium carbonate Ebelmen obtained a product which, after treatment with hydrochloric acid, left a crystalline chromite analogous to Alexandrite.

From crystals of  $\text{BeO}$  prepared by Ebelmen, he obtained parameters  $a : h = 1 : 1.6305$ , isomorphous with  $\text{ZnO}$ , positive and uniaxial. Made artificial phenacite

- $\text{Be}_2\text{SiO}_4$  by fusing silica, beryllia and borax together in optically positive hexagonal prisms.
- 1887; 5. Zimmermann, A. Ueber die Trennung der Thonerde und Beryllerde.  
Inaugural Dissertation, Berlin, 1887.  
Ztschr. f. anorg. Chem., 15, 285.  
Ztschr. f. anal. Chem., 27, 61.  
Chem. News, 58, 49.  
J. Chem. Soc. (Lon.), 54, 323.  
Separated by boiling a solution in KOH. Also recommends separation by boiling with sodium thiosulphate after neutralization with  $\text{Na}_2\text{CO}_3$ . Not new and separations far from perfect.
- 1888; 1. Neumann, G. Ueber Doppelsalze von Sesquichloriden mit anderen Metallchloriden.  
Ann. der Chem. (Liebig.), 244, 335.  
Chem. Centrbl., 1888, 709.  
Made  $\text{BeCl}_2 \cdot \text{FeCl}_3 + \text{H}_2\text{O}$  and  $\text{BeCl}_2 \cdot \text{CrCl}_3 + \text{H}_2\text{O}$   
 $3\text{BeCl}_2 \cdot \text{Ti}_2\text{Cl}_6$ .
- 1888; 2. Kluss, K. Zur Kenntniss der Unterschweifelsauren Salze. Unterschweifelsaures Beryllium.  
Ann. der Chem. (Liebig.), 246, 195.  
Bull. soc. chim., (3) 2, 14.  
 $5\text{BeO} \cdot 2\text{S}_2\text{O}_3 + 14\text{H}_2\text{O}$ . Basic salt, colorless gummy mass. Loses  $\text{H}_2\text{O}$  and  $\text{SO}_2$  on heating. Made by carefully evaporating a solution of  $\text{Be}(\text{OH})_2$  in dithionic acid. (Probably an indefinite solid solution).
- 1888; 3. Sestine, F. Ueber einige selten in Pflanzen vorkommende und seither noch nicht darin gefundene chemische Elemente, Spezielle über Beryllium mit Rücksicht auf einige Kultwerke Pflanzen.  
Chem. Centrbl., 1888, 1622. From.  
Staz. Sperim. Agrar., 15, 290-298.  
Jsb. Chem., 1888, 2556.  
Found beryllium in ash of plants which had been fed with  $\text{BeSO}_4$ , instead of  $\text{MgSO}_4$ . Also in plants from beryllium containing soils.

- 1888; 4. Hautefeuille, P. and Perrey, A. Sur l'action mineral-  
istetrice des sulfures alcalins.

Comptes rend., 106, 487, 1800.

Jsb. Chem., 1888, 555, 557, 558.

Chem. News, 58, 24.

Ztschr. f. Kryst., 18, 322.

Berichte, 21, 175, 599.

Prepared artificial phenacite and emerald.

- 1888; 5. Hautefeuille, P. and Perrey, A. Sur les combinaisons  
silicates de la glucine.

Comptes rend., 107, 786.

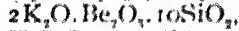
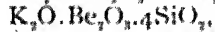
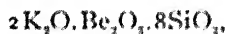
Chem. Centrbl., 1888, 1569.

Ztschr. f. Kryst., 18, 328.

J. Chem. Soc., 56, 104.

Berichte, 21, 887.

If constituents of a beryllium leucite are fused at 600°-800° in excess of potassium vanadate, crystals are obtained of heterogeneous composition and which he concludes may be considered as mixtures of the following:



Claims Be can replace Al in above and also in orthoclase.

- 1889; 1. Stolba, Fr. Aufschliessung des Berylls mit Atzlauge  
Listy chemické, (Prag.), 13, 117.

Chem. Centrbl., 1889, I, 297.

Claimed to act upon finely divided beryl with 10 per cent. NaOH solution so that it was decomposed by HCl.

- 1889; 2. Dana, E. S. and Wells, H. L. New Mineral,  
Beryllonite.

Am. J. Sci., (3) 37, 23-32.

Chem. Centrbl., 1889, I, 141; 1890, I, 337.

Ztschr. f. Kryst., 17, 592.

Gives method of analysis in brief.

- 1889; 3. Mendeléeff. The Periodic Law of the Chemical Elements (Faraday Lecture, June 4, 1889).  
J. Chem. Soc., 55, 650.  
Discussion of the place of beryllium among the elements and the interesting controversy finally settled in favor of the periodic law.
- 1889; 4. Wulff, G. Optische Studien an pseudosymmetrischen Krystallen. Das Beryllium Sulfat.  
Ztschr. f. Kryst., 17, 592.  
Chem. Centrbl., 1890, II, 73.  
Beryllium sulphate is strongly double refractive, is negative and uniaxial.
- 1890; 1. Moraht, Hermann. Untersuchungen über das Beryllium. Inaugural Dissertation, Munich, 1890. See 1890; 5 and 1890; 7.
- 1890; 2. Sestini, Fausto. Proprieta di alcuni sali di berillio e die corrispondenti composti di alluminio.  
Gazzetta chim. ital., 20, 313.  
Chem. Centrbl., 1890 II, 542.  
J. Chem. Soc. (Lon.), 60, 151.  
Berichte, 23, 482.  
J. Russ. Phys. and Chem. Soc., 22, II, 131.  
Rather general work upon the phosphate and carbonate. Obtained a precipitate to which he gave the formula:  $3\text{BeO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O} + \text{Ag}$ . Compared the solubility of  $\text{Be}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$  in carbonated waters. Slightly greater solubility of  $\text{Be}(\text{OH})_2$  in carbonate water.
- 1890; 3. Winkler, Clemens. Ueber die Reduction von Sauerstoffverbindungen durch Magnesium.  
Berichte, 23, 120.  
J. Chem. Soc. (Lon.), 58, 451.  
Reduced (only partially)  $\text{BeO}$  by  $\text{Mg}$ . Reduction very doubtful.
- 1890; 4. Krüss, Gerhard and Moraht, Hermann. Untersuchungen über das Beryllium.  
Berichte, 23, 727.  
Preliminary communication to German Chemical Society. For complete details see 1890; 5.

- 1890; 5. Krüss, Gerhard and Moraht, Hermann. Untersuchung über das Beryllium I.

Ann. der Chem., 260, 161.

Chem. Centrbl., 1890, I, 794, II, 734, 989.

Jsb. Chem., 1890, 538.

Bull. soc. chim., (3) 4, 377, 833.

Chem. News, 65, 12.

J. Chem. Soc. (Lon.), 58, 697.

J. Amer. Chem. Soc., 12, 154.

Ztschr. anal. Chem., 31, 693.

J. Russ. Phys. and Chem. Soc., 22, II, 130.

Prepared impure Be in hexagonal plates by reduction of  $K_2BeF_4$  with sodium.

Made  $Be(OK)_2$  impure which was easily decomposed by  $CO_2$ .

Made  $BeSO_3$  (in absolute alcohol) and gave the formulas  $BeO \cdot BeSO_3$  and  $BeO \cdot 3BeSO_3$  to some basic substances obtained.

Made  $5BeO \cdot B_2O_3$  (dried at  $110^\circ$ ). Research was carried on to show the weak basic character of Be.

- 1890; 6. Krüss, Gerhard and Moraht, Hermann. Untersuchungen über das Beryllium.

Berichte, 23, 2552.

Advance communication of 1890; 7.

- 1890; 7. Krüss, Gerhard and Moraht, Hermann. Untersuchung über das Beryllium, II.

Ann. der Chem., 262, 38-61.

Chem. Centrbl., I, 569.

Jsb. Chem., 1891, 491.

Bull. soc. chim., (3) 8, 51.

Ztschr. phys. Chem., 7, 226.

Chem. News, 67, 242.

J. Chem. Soc., (Lon.), 58, 697; 60, 881.

J. Amer. Chem. Soc., 12, 154.

Ztschr. Anal. Chem., 30, 530.

J. Russ. Phys. and Chem. Soc., 22, II, 132.

Prepared  $BeSO_4 \cdot 4H_2O$  with great care and of a high de-

gree of purity. Material from several sources. Determined the atomic weight by ignition of sulphate after drying over phosphorus pentoxide. Mean of fourteen determinations using large quantities of material gave 9.027 ( $O=16$ ). Specific gravity of  $BeSO_4 \cdot 4H_2O$  found to be 1.7125. Specific gravity  $BeO=2.9644$ .

1.7125. Specific gravity  $BeO=2.9644$ .

- 1890; 8. Petersen, Emil. Neutralisationsphänomene des Aluminium und Beryllium Fluorid.

Ztschr. phys. Chem., 5, 259-266.

Chem. Centrbl, 1890, I, 892.

Berichte, 23, 270.

J. Chem. Soc. (London), 58, 680.

Heat of neutralization of  $Be(OH)_2 + 2HF.Aq = 19683$  calories.

- 1890; 9. Hautefeuille, P. and Perrey, A. Sur la cristallization de l'alumine et de la glucine.

Bull. de la soc. franc. de min., 13, 149.

Ztschr. f. Kryst., 21, 306.

J. Russ. Phys. and Chem. Soc., 22, II, 133.

Chem. Centrbl., 1890, II, 716.

Prepared crystals of beryllium oxide, by dissolving the oxide in fused leucite. Also prepared chrysoberyl.

- 1890; 10. Hautefeuille, P. and Perrey, A. Sur les silico glucinates de soude.

Comptes rend., 110, 344.

Jsb. Chem., 1890, 143.

Chem. Centrbl., 1890, I, 668, II, 716.

J. Chem. Soc. (London), 58, 562.

Berichte, 23, 288.

On fusing a mixture of  $BeO$ ,  $SiO_2$  and  $Na_2O$  (in same proportion as in a beryllium nephylene) in excess of sodium vanadate at about  $800^\circ C.$ , crystals to which they gave the following formula,  $Na_2O$ ,  $Be_2O_3$ ,  $3SiO_2$  were obtained. Also obtained substances to which they assigned the following formulas:

$Na_2O$ ,  $Be_2O_3 \cdot 6SiO_2$ ,



$2\text{Na}_2\text{O}, 3\text{Be}_2\text{O}_3, (20.67-22.41) \text{SiO}_2,$

$3\text{Na}_2\text{O}, 2\text{Be}_2\text{O}_3, 15\text{SiO}_2,$

$3\text{Na}_2\text{O}, 2\text{Be}_2\text{O}_3, 18\text{SiO}_2,$

$3\text{Na}_2\text{O}, 2\text{Be}_2\text{O}_3, 14\text{SiO}_2.$

- 1890; 11. Ouvrard, L. Sur quelques phosphates de lithine, de glucine, de plomb et d'urane.

Comptes rend., **110**, 1333-36.

Chem. Centrbl., **1890**, II, 203.

Chem. News., **62**, 25.

Bull. soc. chim., (3) **5**, 80.

J. Chem. Soc. (London), **58**, 1055.

Berichte, **23**, 550.

By fusing with potassium, meta, pyro and orthophosphate, obtained  $\text{K}_2\text{O} \cdot 2\text{BeO} \cdot \text{P}_2\text{O}_5$  in rhombic prisms. With sodium meta and pyrophosphate, obtained  $\text{Na}_2\text{O} \cdot 2\text{BeO} \cdot \text{P}_2\text{O}_5$ , in hexagonal plates identical with beryl-lonite. From sodium orthophosphate  $2\text{Na}_2\text{O} \cdot \text{BeO} \cdot \text{P}_2\text{O}_5$  in lamellae.

- 1890; 12. Wagner, J. Untersuchung über die innere Reibung von Flüssigkeiten.

Ztschr. phys. Chem., **5**, 34.

Uses  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  as one of the salts of the series studied.

- 1890; 13. Rydberg, J. R. Ueber den Bau der Linienspektren der chemischen Grundstoffe.

Ztschr. phys. Chem., **5**, 231.

Refers in discussion to lines for beryllium.

- 1890; 14. Hautefeuille, P. and Perry, A. Über verschiedene Silikatverbindungen der Oxyde von Kobalt, Zinc, Magnesium and Beryllium.

Chem. Centrbl., **1890**, II, 716.

Bull. de la soc. franc. de min., **13**, 149.

By fusing beryllium sulphate with silicic acid obtained hexagonal crystals of beryllium oxide. Also obtained phenacite and a silicate of the composition,  $3\text{BeO} \cdot 2\text{SiO}_2$ .

- 1891; 1. Roozeboom, H. W. Bakhuis. Ueber die Löslichkeit von Mischkrystallin.  
Ztschr. phys. Chem., 8, 528.  
Discussion of the significance of the mixed crystals of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  and  $\text{BeSeO}_4 \cdot 4\text{H}_2\text{O}$ .
- 1891; 2. Behrens, H. Beiträge zur mikrochemischen Analyse.  
Ztschr. f. Anal. Chem., 30, 139.  
Chem. News, 64, 41.  
Detects beryllium by means of the crystals of its double oxalate with potassium.
- 1891; 3. Winkler, Clemens. Ueber die Reduction von Sauerstoffverbindungen durch Magnesium.  
Berichte, 24, 1966.  
Bull. soc. chim., (3) 6, 724.  
J Chem. Soc. (London), 60, 1155.  
Claimed to make a very impure  $\text{BeH}$  by heating a mixture of  $\text{BeO}$  and  $\text{Mg}$  in  $\text{H}$  for four hours. Results rather uncertain.
- 1891; 4. Rammelsberg, C. Ueber einige Salze der Unterphosphorsäure.  
Sitzber. Akad. Wiss. (Berlin), 1891, 369-76.  
J. prakt. Chem., (2) 45, 158.  
Chem. Centrbl., 1891, II, 790.  
Bull. soc. chim., (3) 8, 686.  
J. Chem. Soc. (London), 62, 404.  
Hot solution of  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  when precipitated with normal  $\text{Na}_2\text{PO}_3$ , yields  $2\text{BePO}_3 + 3\text{H}_2\text{O}$  which loses  $\frac{1}{2}$  of its water at  $230^\circ$ - $250^\circ$ .
- 1891; 5. Jahn, Hans. Ueber die electromagnetische Drehung der Polarizationsebene in Flüssigkeiten, besonders in Salzlösungen.  
Ann. der Phys. (Wied), 43, 284.  
Found the specific rotation for  $\text{BeSO}_4 = 0.28895$ .
- 1891; 6. Sestini, Fausto. Experiments with wheat on the substitution of Beryllium for Magnesium.

J. Chem. Soc. (London), abs. from Staz. sperim. agrar. Ital., 20, 256.

Jsb. Chem., 1891, 2702.

Experiments indicate that beryllium may take the place of magnesium in growth of wheat but is not a complete substitute for magnesium in production of seed.

- 1892; 1. Friedel, Ch. and Sarasin. Production artificielle de divers mineraux.

Bibliothique Universelle, Arch. phys. nat., 27, 145.

Chem. Centrbl., 1892, I, 864.

Jsb. Chem., 1892, 520.

Obtained a beryllium aluminum potassium silicate by fusing the oxide of the first two with potassium silicate.

- 1892; 2. Rauter, Gustav. Ueber das Siliciumtetrachlorid.

Ann. der Chem., 270, 244.

Jsb. Chem., 1892, 645.

Heated  $\text{SiCl}_4$  and powdered metallic beryllium in a closed tube for three hours at  $240^\circ$ - $250^\circ$  and found that a partial double decomposition took place yielding as a result a mixture of  $\text{SiCl}_4$ ,  $\text{BeCl}_2$ , Be and Si.

- 1892; 3. Grätzel von Grätz, A. Verfahren zur Gewinnung von Bor, Silicium, Aluminium, Beryllium und Magnesium.

D. Pat., 58600.

Chem. Ind., 14, 499.

Ding. polyt. J., 283, 129.

Jsb. Chem., 1892, 2651.

Proposes to mix the oxide of beryllium with the chloride of a more electro positive element and by passing current to obtain metal at one pole and oxygen at the other.

- 1892; 4. McMahon, C. A. Microchemical Analyses of rock forming mineral.

Min. Mag. and J. of Min. Soc., 10, 79-122.

Says the double salt  $\text{BeK}_2(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$  is very characteristic. Does not use the oxalate as recommended by Behrens (1891; 2).

- 1892; 5. Karnojitsky, A. Ueber die optische Anomalie des Beryls.  
Ztschr. f. Kryst., 19, 209-219.  
Chem. Centrbl., 1892, I, 492.  
Studied the optical properties of beryl.
- 1892; 6. Schleir, M. Zur Anwendung des Nitroso- $\beta$ -Naphthols in der quantitative Analyse. Trennung von Eisen und Berylliums.  
Chem. Ztg., 16, 420.  
Chem. Centrbl., 1892, I, 717.  
Jsb. Chem., 1892, 2540.  
Ztschr. f. anorg. Chem., 3, 84.  
Ztschr. anal. Chem., 36, 699.  
Gives details for analysis of a mixture of iron and beryllium salts by precipitating the former with nitroso- $\beta$ -naphthol. Excellent quantitative results obtained. Says that it is the best method of removing last trace of iron from beryllium.
- 1893; 1. Hautefeuille, P. and Perrey, A.  
Annales de chim. et de phys., (6) 20, 447-474.  
Artificially produced phenacite, beryl and a number of uncertain sodium and potassium beryllium silicates and basic beryllium silicates.
- 1893; 2. v. Helmholt, Hans. Ueber Einige Doppelfluoride.  
Ztschr. f. anorg. Chem., 3, 115-152.  
Jsb. Chem., 1893, 409.  
Obtained  $\text{BeF}_2 \cdot 2\text{NH}_4\text{F}$  in fine crystals. Crystallizes in small colorless needles and prisms. Prepared by dissolving  $\text{Be}(\text{OH})_2$  in  $\text{H}\text{NH}_4\text{F}$  to saturation and evaporating.
- 1893; 3. Gibson, John.  
J. Chem. Soc. (London), 63, 909.  
Chem. Centrbl., 1893, I, 512, II, 319.  
Jsb. Chem., 1893, 474.  
Chem. News, 67, 66.  
Chem. Ztg., 17, 210.

Ztschr. anorg. Chem., 5, 240.

Bull. soc. chim., 12, 117.

J. Russ. Phys. and Chem. Soc., 25, II, 165.

Recommends the preparation of BeO by igniting beryl with ammonium hydrogen fluoride, which takes place at a low temperature, and dissolving out with water.

- 1893; 4. Seubert, Karl and Elten, M. Zur Kenntniss der basischen Metallsulfite.

Ztschr. f. anorg. Chem., 4, 52-74, 78-81.

Jsb. Chem., 1893, 312.

J. Chem. Soc. (London), 64, 456.

Made a basic sulphite which came near the formula  $2\text{BeSO}_3 \cdot 9\text{Be}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$  and a basic carbonate  $\text{BeCO}_3 \cdot 5\text{Be}(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ .

- 1894; 1. Traube, H. Ueber die Kunstliche Darstellung des Beryll.

Jahrb. f. Min., 1894, 1; Mem., 275.

J. Chem. Soc. (London), 66, 284.

Added sodium silicate to a solution containing 3 mols  $\text{BeSO}_4$  and one mol  $\text{Al}_2(\text{SO}_4)_3$  and fused the dried precipitate so obtained with  $\text{B}_2\text{O}_3$  in platinum crucible at  $1700^\circ$  for three days. Obtained beryl crystals.

- 1894; 2. Smith, Edgar F. and Heyl, Paul. Ueber die Verwendung von Quicksilber Oxyd bei der Analyse.

Ztschr. f. anorg. Chem., 7, 88.

Could not separate Fe and Al quantitatively from beryllium by  $\text{HgO}$ .

- 1894; 3. Traube, H. Das atomare und molecular Lösungsvolumen.

Ztschr. f. anorg. Chem., 8, 12.

Berichte, 27, 3173-78.

J. Chem. Soc. (London), 68, II, 70.

Molecular solutions volume of  $\text{BeSO}_4$  and  $\text{Be}(\text{ClO}_3)_2$ .

- 1894; 4. Borchers, W. Apparate zur Abscheidung von Magnesium, Lithium und Beryllium aus geschmolzenen Haloidsalzen.

- Ztschr. Elektrotech and Elektrochem., 1894, 361.  
Chem. Centrbl., 1895, I, 579.
- 1894; 5. Wyruboff, G. Silicotungstates.  
Bull. soc. chim., (3) 11, 1106.  
Preliminary note of work on silicotungstates in which he argues for trivalency of beryllium.
- 1894; 6. Combes, Alph. Sur la valence der glucinium et la formule de la glucine.  
Comptes rend., 119, 1221.  
Mon. sci., (4) 9, 154.  
Ztschr. anorg. Chem., 9, 245.  
Chem. News, 71, 38.  
Chem. Centrbl., 1895, I, 320.  
J. Chem. Soc. (London), 68, 224.  
Berichte, 28, 10.  
Bull. soc. chim., (3) 13, 3.  
Made beryllium acetylacetonate,  $\text{Be}(\text{C}_5\text{H}_7\text{O}_2)_2$ , by action of acetyl acetone on beryllium acetate and gives its properties. Melts at 108, sublimes as low as 100°, boils at 270 without decomposition. Two determinations of density gave figures in accord with divalency of beryllium.
- 1894; 7. Walden, P. Ueber die optische Drehung der Ionen.  
Ztschr. phys. Chem., 15, 202.  
Made  $\text{Be}(\text{C}_{10}\text{H}_{14}\text{BrO}.\text{SO}_2.\text{O})_2$ , beryllium alpha brom camphor sulphonate and studied its optical rotation in comparison with similar salts of Mg, Zn, and Ba in dilute solution. Found the rotation essentially the same for all (compare 1899; 13) and for the acid itself. These ions therefore inactive.
- 1895; 1. Wyruboff, G. Response to remarks of A. Combes on valence of beryllium.  
Bull. soc. chim., (3) 13, 4.
- 1895; 2. Lebeau, P. Sur un carbure du glucinium.  
Comptes rend., 121, 496.  
Ztschr. anorg. Chem., 13, 364.  
Chem. Centrbl., 1895, II, 959.

Bull. soc chim., (3) 13, 1065.

Chem. News, 72, 209.

Mon. sci., (4) 9, 806.

Ztschr. f. Elektrochem., 2, 409.

J. Soc. Chem. Ind., 15, 141.

J. Chem Soc. (London), 70, 169.

Berichte, 28, 899.

BeO mixed with half its weight of sugar carbon and a little oil and heated in an electric furnace for 8-10 minutes with 950 amperes at 40 volts. Obtained carbide which he calls  $\text{Be}_4\text{C}_3$  (which was undoubtedly  $\text{Be}_2\text{C}$ ) in crystals, harder than quartz, transparent. Specific gravity 1.9 at 15°. Attacked at red heat by Cl, Br, HF, and HCl with liberation of carbon and formation of halide. Slowly decomposed water, liberating  $\text{CH}_4$ . Quickly decomposed by caustic alkalies. No other carbide seems to exist.

1895; 3. Lebeau, P. Sur l'analyse de l'emeraude.

Comptes rend., 121, 601.

Chem. News, 72, 245.

Dissolved in KOH in silver crucible and afterward followed procedure of Debray.

1895; 4. Rowland, H. A. and Tatnall, R. R. The arc spectra of the elements. II. Boron and Beryllium.

Astrophysical Journal, 1895, I, 16; II, 185.

Gives as the most prominent lines for Be between 2100 and 4600 the following:

2348.697

2350.855

2494.532

2494.960

2650.414

2651.042

3130.556

3131.200

3321.218

3321.486

4572.869

Observations made by means of a grating of  $21\frac{1}{2}$  feet radius and 20000 lines to the inch on photographic plate 19 inches in length.

- 1895; 5. Lebeau, P. Sur la traitement de l'émeraude et la préparation de la glucine pure.

Comptes rend., 121, 641.

Ztschr. anorg. Chem., 13, 364.

Bull. soc. chim., (3) 15, 166.

Chem. News, 73, 3.

Mon. sci., (4) 10, 71.

Ztschr. f. Elektrochem., 2, 432.

Chem. Centrbl., 1895, II, 1150.

J. Chem. Soc. (London), 70, 168.

Decomposed beryl by fusion with twice its weight of  $\text{CaF}_2$ , when on pouring into water, a friable mass, easily attacked by  $\text{H}_2\text{SO}_4$ , was obtained. Most of the silica was thereby removed. Also fused beryl in an electric furnace and volatilized part of its silica when residue was easily attacked by a mixture of  $\text{H}_2\text{SO}_4$  and HF. Impure beryllium carbonate obtained by usual procedure was dissolved in  $\text{HNO}_3$ , iron precipitated by ferrocyanide, the excess ferrocyanide by copper nitrate and the copper by  $\text{H}_2\text{S}$ . The solution was then mixed with ammonia and the precipitate allowed to stand three days whereby the  $\text{Al}(\text{OH})_3$  became insoluble in ammonium carbonate.

- 1895; 6. Hart, Edward. Note on the Purification of Glucinium Salts.

J. Amer. Chem. Soc., 17, 604.

Chem. Centrbl., 1895, II, 590.

Bull. soc. chim., (3) 16, 226.

Chem. News, 72, 77.

J. Chem. Soc. (London), 70, 168.

Separates beryllium from iron and aluminum by dissolving in  $\text{H}_2\text{SO}_4$  and adding  $\text{Na}_2\text{CO}_3$  slowly, with boiling after each addition, until the liquid shows no yellow color. The beryllium remains in solution as a basic sulphate while the iron and aluminum are precipitated.



- 1895; 7. Prudhomme, Maurice. Sur le mordant de glucine.  
Bull. soc. chim., (3) 13, 509.  
Mon. sci., (4) 9, 411.  
Ztschr. f. anorg. Chem., 10, 446.  
Chem. Centrbl., 1895, II, 264.  
J. Soc. Chem. Ind., 14, 802.  
Beryllium acts as a divalent, not as a trivalent element.
- 1895; 8. Henry Louis. Apropos un carbure du glucinium.  
Comptes rend., 121, 600.  
Ztschr. f. anorg. Chem., 13, 365.  
Bull. soc. chim., 15, 165, 475.  
Chem. Centrbl., 1895, II, 1067.  
Bull. acad. Belg., 30, 460-465.  
Chem. News, 72, 245.  
J. Chem. Soc. (London), 70, 169.  
Mon. sci., (4) 9, 857.  
Berichte, 28, 967.  
J. Soc. Chem. Ind., 15, 141.  
Criticises Lebeau (1895; 2) for giving formula  $\text{Be}_4\text{C}_3$  to his carbide and using atomic weight of 13.8 when analyses agreed with  $\text{Be}_2\text{C}$  and valency of beryllium had been proven.
- 1895; 9. Atkinson, E. A. and Smith, E. F. The Separation of Iron from Beryllium.  
J. Amer. Chem. Soc., 17, 688.  
Chem. Centrbl., 1895, II, 844.  
Bull. soc. chim., (3) 16, 229.  
Ann. de chim. analytique, 1, 118.  
J. Chem. Soc. (London), 70, 220.  
Analyst, 21, 23.  
Showed that iron and beryllium can be quantitatively separated by Nitroso- $\beta$ -Naphthol. (Compare 1892; 6).
- 1895; 10. Warren, H. N. Manufacture and Commerical Separation of Glucinium.  
Chem. News, 72, 310.  
Ztschr. f. anorg. Chem., 13, 364.  
Ztschr. f. Elektrochem., 2, 459.

Chem. Centrbl., 1896, I, 336.

J. Chem. Soc. (London), 70, 247.

Proposed separation of the metal by electrolytic reduction of the bromide. Bromide, however, is a non conductor.

11. Borchers, W. Abschiedungsmethoden des Lithiums und des Berylliums.

Ztschr. f. Elektrochem, 2, 3, 9.

Chem. Centrbl., 1895, II, 13.

J. Chem. Soc. (London), 70, 521.

Ztschr. phys. Chem., 21, 517.

Proposes to electrolyze a melted mixture of  $\text{BeCl}_2$  with alkaline chlorides or alkaline earth chlorides. Makes mixture by evaporating mixed chlorides and adding a little  $\text{NH}_4\text{Cl}$  to arrest conversion of  $\text{BeCl}_2$  into  $\text{BeO}$ . Calcium and magnesium chlorides must be absent. No metal appears to have been made.

12. Rinne, F. Die Krystallform chemischen einfacher Korper.

Ztschr. phys. Chem., 16, 529.

Gives crystal form data for Be and  $\text{BeO}$  in table with many other substances.

1. Wyruboff, G. Silicotungstates.

Bull. soc. franc. d. min., 19, 219, 354.

Ztschr. f. Kryst., 29, 676.

J. Chem. Soc. (London), 72, 178.

Made beryllium silico tungstate to which he gave the formula  $\text{Be}_4(\text{W}_{12}\text{SiO}_{40})_3$ . Crystallizes below  $45^\circ$  as a cubic hydrate containing 93  $\text{H}_2\text{O}$ ; above  $45^\circ$ , as a rhombohedral hydrate containing 87  $\text{H}_2\text{O}$ . In presence of nitric acid at  $30^\circ$  a 45  $\text{H}_2\text{O}$  is obtained.

2. Properties of Beryllium.

Eng. and Mining J., 6, 162 from Electrical Review of London.

Revue de chim. ind., 7, 323.

Claims beryllium is on the market at \$18 a pound and gives very improbable properties for metal.

- 1896; 3. Liebermann, Louis. Verfahren zur Darst. von Beryllium in form seiner Legierungen.

D. R. P. 94507, Sept. 22, '96, Patent bl. 18868.

Chem. Ztg., 23, 253.

Berg. in Hutten Ztg., 57, 149.

Wagners Jsb., 43, 320.

Ztschr. f. Elec., 4, 258.

- 1896; 4. Retgers, J. W. Beiträge zur Kenntniss des Isomorphismus.

Ztschr. f. phys. Chem., 20, 481.

Ztschr. f. Kryst., 30, 635.

Amer. J. Sci., (4) 2, 448.

J. Chem. Soc. (London), 72, 17.

Berichte, 29, 1059.

By discussion of the results of others and by crystallizing mixtures of the sulphates of Cu, Ni, Fe, Mn and Be, Retgers comes to the conclusion that Be is not isomorphous with the metals of the Mg. group.

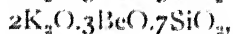
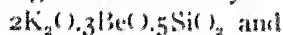
- 1896; 5. Duboin, André. Sur une methode de reproduction de silicates doubles de potasse et d'autres bases.

Comptes rend., 123, 698.

Chem. Centrbl., 1896, II, 1081.

J. Chem. Soc. (London), 72, 96.

Obtained crystals of a double silicate of Be and K which appear homogeneous but vary between



made by dissolving a mixture of BeO and SiO<sub>2</sub> in fused KF and then submitting to long fusion with KCl.

- 1896; 6. Lebeau, P. Sur quelques propriétés de la glucine pure.

Comptes rend., 123, 818.

Chem. Centrbl., 1897, I, 16.

Ztschr. anorg. Chem., 15, 472.

Chem. Ztg., 20, 973; 21, 8.

Chem. News, 74, 292.

- J. Soc. Chem. Ind., **16**, 72.  
J. Chem. Soc. (London), **72**, 144.  
J. Russ. Phys. and Chem. Soc., **29**, **11**, 58.  
Specific gravity BeO ignited at  $440^{\circ}$  = 3.012, ignited at  $1200^{\circ}$  = 3.01.  
BeO fuses in electric arc and on cooling forms a white crystalline mass, slightly harder than rubies. BeO is attacked by fluorine when heated but not by other halogens or by sulphur or nitrogen.  
Potassium, sodium and aluminum have no action on the oxide at high temperatures and it is not reduced by magnesium even at the boiling point of that metal.  
BeO swells up in pure  $\text{H}_2\text{SO}_4$  and yields anhydrous sulphate which dissolves very slowly in boiling  $\text{H}_2\text{O}$ .
- 1896; 7. Burgass Rob. Anwendung des Nitroso- $\beta$ -Naphthols in der anorganische Analyse.  
Ztschr. angewdte. Chem., **1896**, 596.  
J. Chem. Soc. (London), **72**, 163.  
Separates quantitatively iron from beryllium by means of Nitroso- $\beta$ -Naphthol.  
Compare 1892; 6 and 1895; 9.
- 1896; 8. Glaser, Charles. Chemical Analysis of Monazite Sand.  
J. Amer. Chem. Soc., **18**, 782  
J. Chem. Soc. (London), **72**, 191.  
Rev. Amer. Chem. Research, **2**, 66.  
Gives his method for determining beryllium in monazite.
- 1896; 9. Anonymous.  
Beryllium instead of platinum for incandescent lamps.  
Elektrochem. Ztschr., **3**, 70, from Journal des inventeurs.  
Suggests use as indicated by title. Coefficient of expansion not given.
- 1896; 10. Larssow, Aksel. Untersuchung über Niob.  
Ztschr. f. anorg. Chem., **12**, 188.  
J. Chem. Soc. (London), **70**, 564.

Made a crystalline beryllium columbate by fusing with boric anhydride. the precipitate obtained by precipitating potassium columbate with beryllium chloride.  
Found composition, 6.24 per cent.  $\text{BeO}$ , 89.60 per cent.  $\text{Cb}_2\text{O}_6$ .

- 1896; 11. Gladstone, J. H. The Relation between the refraction of elements and their chemical equivalents.  
Proc. Roy. Soc., 60, 140-146.  
Ztschr. phys. Chem., 22, 648.  
Specific refraction  $\text{Be} = .733$ .  
Atomic refraction  $\text{Be} = 6.6$ .
- 1896; 12. Ortloff, W. Beitrage zur Kenntniss eutropischer Reihen.  
Ztschr. phys. Chem., 19, 201.  
Quote physical properties in discussion.
- 1897; 1. Havens, Franke S. The Separation of Aluminium and Beryllium by the action of Hydrochloric Acid.  
Amer. J. of Sci., (4) 4, 111-114.  
Chem. Centrbl., 1897, II, 810.  
Bull. soc. chim., (3) 18, 1129.  
Chem. News, 76, 111 (complete).  
Analyst, 23, 109.  
Separates Be and Al quantitatively by means of the insolubility of  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  in ether and water (1:1), saturated with HCl gas.
- 1897; 2. Havens, Franke S. Trennung von Aluminium und Beryllium durch Salzsäure.  
Ztschr. anorg. Chem., 16, 15-18.  
Chem. Centrbl., 1898, I, 476.  
Bull. soc. chim., (3) 26, 163.  
J. Chem. Soc. (London), 74, 142.  
Same as 1897; 1.
- 1897; 3. Woge, Paul. Ueber die Wertigkeit des Berylliums. Inaugural Dissertation, (Berlin), 1897.  
See 1897; 4.

- 1897; 4. Rosenheim, A. and Woge, P. Ueber die Wertigkeit des Berylliums.

Ztschr. f. anorg. Chem., 15, 283-318.

Bull. soc. chim., (3) 20, 308.

J. Phys. Chem., 2, 400.

Chem. Centrbl., 1897, II, 1131.

Chem. News, 78, 160.

J. Chem. Soc. (London), 74, 71.

Extensive research on the oxalates, tartrates, molybdates and sulphites of beryllium to show their differences from the corresponding salts of Al, Fe and Cr, ending with the preparation of  $\text{BeCl}_2$  and the determination of its molecular weight in pyridine by the boiling point method.

The following substances were prepared:

$\text{K}_2\text{O}, 2\text{BeO}, 2\text{C}_2\text{O}_3 + 2\frac{1}{2}\text{H}_2\text{O},$	} These were obtained in crystalline forms and seem to be definite basic compounds,
$\text{Na}_2\text{O}, 2\text{BeO}, 2\text{C}_2\text{O}_3 + 5\text{H}_2\text{O},$	
$(\text{NH}_4)_2\text{O}, 2\text{BeO}, 2\text{C}_2\text{O}_3 + 2\frac{1}{2}\text{H}_2\text{O},$	
$\text{K}_2\text{O}, \text{BeO}, 2\text{C}_2\text{O}_3 + \text{H}_2\text{O},$	
$\text{Na}_2\text{O}, \text{BeO}, 2\text{C}_2\text{O}_3 + \text{H}_2\text{O},$	
$(\text{NH}_4)_2\text{O}, \text{BeO}, 2\text{C}_2\text{O}_3,$	
$2\text{BeO} \cdot 3\text{C}_2\text{O}_3 + 6\text{H}_2\text{O},$	
$\text{BeC}_2\text{O}_4 + 3\text{H}_2\text{O},$	
$\text{K}_2\text{O}, 4\text{BeO}, 2\text{C}_4\text{H}_4\text{O}_5 + 8\text{H}_2\text{O},$	
$\text{Na}_2\text{O}, 4\text{BeO}, 2\text{C}_4\text{H}_4\text{O}_5 + 8\text{H}_2\text{O},$	
$(\text{NH}_4)_2\text{O}, 4\text{BeO}, 2\text{C}_4\text{H}_4\text{O}_5 + 8\text{H}_2\text{O},$	
$\text{K}_2\text{O}, 2\text{BeO}, 2\text{C}_4\text{H}_4\text{O}_5 + 2\text{H}_2\text{O},$	
$\text{BeO}, \text{MoO}_3, 2\text{H}_2\text{O},$	
$10(2\text{BeO} \cdot \text{MoO}_3) + 2(\text{NH}_4)_2\text{O}, 3\text{MoO}_3 + 18\text{H}_2\text{O},$	
$\text{K}_2\text{O}, 2\text{BeO}, 3\text{SO}_2 + 9\text{H}_2\text{O},$	
$(\text{NH}_4)_2\text{O}, 2\text{BeO}, 3\text{SO}_2 + 4\text{H}_2\text{O}.$	

- 1897; 5. Heusler, Fr. Die Chemie bei der Temperature des elektrischen Lichtbogens.

Ztschr. anorg. Chem., 14, 173.

Compilation of the work on carbides including that of beryllium.

- 1897; 6. Gladstone, J. H. and Hibbert, W. The Molecular Refraction of dissolved Salts and Acids.

J. Chem. Soc. (London), 71, 823.

Compared the molecular refraction of solid and dissolved  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$ .

Molecular refraction of solid 47.41.

Molecular refraction of liquid 47.94.

- 1897; 7. Mosnier, A. Sur quelques combinaisons de l'iodure de plomb avec d'autres iodures métalliques ou organiques. Iodure double de plomb et de glucinium.

Ann. de chim. et de phys., (7) 12, 374 (2°).

J. Chem. Soc. (London), 76, 222.

Treated carbonate of beryllium with concentrated HI, then added lead iodide as long as it dissolved. By cooling, obtained fine yellow needles decomposed by water. From analysis he calculates the formula  $\text{Be}_2\text{I}_{10} \cdot 3\text{PbI}_2 \cdot 10\text{H}_2\text{O}$ .

- 1897; 8. Lebeau, P. Sur la préparation des alliages de glucinium. Alliages de glucinium et de cuivre.

Comptes rend., 125, 1172.

Bull. soc. chim., (3) 19, 54.

Chem. Centrbl., 1898, I, 310.

Chem. Ztg., 22, 17.

Ztschr. anorg. Chem., 19, 351.

J. de pharm. et de chim., (6) 7, 240.

Chem. News, 77, 44.

J. Chem. Soc. (London), 74, 292.

J. Soc. Chem. Ind., 17, 1152.

Owing to the ease with which Be and C combine at high temperatures, the metal can not be reduced from its oxide in the electric arc. Alloys can be prepared however, by reducing BeO in this manner in contact with other metals or metallic oxides. Prepared alloys with Cu, Cr, Mo and W, but describes those of copper only. With 10 per cent. of Be the copper alloys are pale yellow, almost white. With 5 per cent. Be they are yellow, easily polished and malleable cold or hot. As low as 5 per cent. Be alters appearance of Cu and makes it sonorous. Alloy of 1.32 per cent. is golden yellow and can be easily filed and forged.

- 1898; 1. Lebeau, P. Recherches sur le glucinium et ses composés.  
Academic Dissertation, Paris, 1898.
- 1898; 2. Lebeau, P. Sur un procédé de preparation des bronzes de glucinium.  
Bull. soc. chim., (3) 19, 64.  
Chem. Centrbl., 1898, I, 496.  
See 1897; 8.
- 1898; 3. Lebeau, Paul. Preparation du glucinium par electrolyse.  
Comptes rend., 126, 744.  
Chem. Centrbl., 1898, I, 879.  
Chem. News, 77, 173.  
J. Phys. Chem., 3, 185.  
Amer. J. Sci., (4) 7, 155.  
Zeit. f. Elec., 5, 31.  
Bull. soc. chim., (3) 19, 409.  
Chem. Ztg., 22, 245.  
J. Chem. Soc. (London), 74, 511.  
J. de phar et de chim., (6) 7, 345.  
J. Soc. Chem. Ind., 17, 386.  
Obtained metallic beryllium by electrolysis of  $\text{BeF}_2 \cdot \text{NaF}$  in nickel crucible. Melted over bunsen burner and then passed current of 6-9 amperes at 35-40 volts removing source of heat. Made salt by fusing exact equivalents 1-1 of the two fluorides. Nickel crucible negative pole and graphite stick positive pole.
- 1898; 4. Lebeau, Paul. Gewinnung von Beryllium durch Electrolyse. Beryllium Legierungen.  
Elektrochemische Zeitschrift, 5, 111.  
Chem. Centrbl., 1898, II, 750.  
J. Soc. Chem. Ind., 17, 155.  
Amer. Chem. J., 27, 487.  
Article is fully as complete as 1898; 3 and much the same in character although a separate communication. Says Nilson and Petterssen found  $\text{BeCl}_2$  to be a non-conductor, which he confirmed and found same to be



true of the bromide and fluoride. Added NaF to make mixture conduct electricity. Used nickel crucible and carbon anode with a current of 20 amperes and 80 volts (vide 1898; 3). Heated first with bunsen burner but later controlled heat by current alone. Kept at low redness. Fine hexagonal Be obtained free from iron and nickel with a specific gravity of 1.73 at 15°. Gives properties of beryllium.

Made alloys with copper and gives their properties. One-half per cent. Be makes copper quite sonorous. 1.32 per cent. Be in copper is a gold yellow metal and finely sonorous.

- 1898; 5. Lebeau, Paul. Sur le traitement industriel de l'émeraude au feu électrique.

Comptes rend., 126, 1202.

Bull. soc. chim., (3) 19, 940.

Ztschr. f. Elek., 5, 39.

Chem. News, 77, 285.

Chem. Ztg., 22, 380.

Heated beryl in carbon tube in electric furnace at 95 amperes and 50 volts for ten minutes and dissolved in hydrofluoric acid. This removes silicon and aluminum since  $\text{AlF}_3$  is insoluble. Solution worked up for beryllium as ordinarily.

- 1898; 6. Lebeau, Paul. Sur l'iodure de glucinium.

Comptes rend., 126, 1272.

Bull. soc. chim., (3) 19, 800.

Chem. Centrbl., 1898, II, 85.

Ztschr. phys. Chem., 28, 570.

Chem. News., 77, 266.

J. phar. chim., (6) 7, 592.

J. Chem. Soc. (London), 74, 580.

Made  $\text{BeI}_2$  by action of iodine on the carbide and studied its properties exhaustively.

Specific gravity 4.20, fuses at 510° and begins to sublime at once, boils 585-595°.

Insoluble in benzine and toluene, soluble in carbon disulphide.

Attacked violently by water and decomposed by flourine, chlorine and bromine.

- 1898; 7. Lebeau, Paul. Sur un borocarbure de glucinium.

Comptes rend., 126, 1347.

Bull. soc. chim., (3) 19, 823.

Chem. Centrbl., 1898, II, 86.

Chem. Ztg., 22, 425.

Ztschr. f. Elek., 5, 91.

Chem. News, 77, 289, (complete).

J. Chem. Soc. (London), 74, 581.

Prepared  $3\text{Be}_2\text{C} \cdot \text{B}_2\text{O}_3$  by heating a mixture of BeO and B in a carbon crucible in the electric furnace. Crystalline with specific gravity of 2.4.

- 1898; 8. Lebeau, Paul. Sur la préparation et les propriétés du fluorure de glucinium anhydre et de l'oxyfluorure de glucinium.

Comptes rend., 126, 1418.

Bull. soc. chim., (3) 19, 824.

Chem. News, 77, 288, (complete).

Ztschr. f. Elek., 5, 118.

Made  $\text{BeF}_2$  by evaporating a solution of  $\text{Be}(\text{OH})_2$  in excess of HF and drying in HF gas in platinum tube, obtaining thereby a transparent glassy, deliquescent fluoride. If he raised heat to drive off all the water, he obtained a basic residue of approximate  $5\text{BeF}_2 \cdot 2\text{BeO}$  but different analyses did not agree closely. Made purest  $\text{BeF}_2$  by heating  $\text{BeF}_2 \cdot \text{NH}_4\text{F}$  in platinum tube in  $\text{CO}_2$  gas. Anhydrous, glassy, sublimes in little transparent crystals above  $800^\circ$ , specific gravity 2.1. Soluble in  $\text{H}_2\text{O}$  and in 90 per cent. alcohol. Attacked by  $\text{H}_2\text{SO}_4$ .

- 1898; 9. Höber, Rudolf and Kiesow, Friedrich. Ueber den Geschmack von Salzen und Laugen.

Ztschr. phys. Chem., 27, 601.

Chem. Centrbl., 1899, I, 332.

Found that  $\text{BeCl}_2$  and  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  have the same sweet taste at equal cation concentrations.

- 1898; 10. Boudard, O. Sur les sables monazites de la Carolina du Nord.

Bull. soc. chim., (3) 19, 10.

Chem. Centrbl., 1898, I, 435.

Gives method of analyzing monazite including separation of beryllium.

- 1898; 11. de Gramont, A. Analyse spectrale des minéraux nonconducteurs par les sels fondus.

Bull. de la soc. franc. de min., 21, 100.

Comptes rend., 126, 1513.

Ztschr. f. Kryst., 32, 637.

J. Chem. Soc. (London), 74, 636.

Obtains the blue line, 457.3 easily in spark spectra by fusing beryl with lithium carbonate.

- 1898; 12. Curtius and Rissom. Neue Untersuchungen über den Stickstoffwasserstoff  $\text{N}_3\text{H}$ .

J. f. prakt. Chem., 58, 292.

J. Chem. Soc., 76, 92.

Attempts to make  $(\text{N}_3)_2\text{Be}$  by action of  $(\text{N}_3)_2\text{Ba}$  upon  $\text{BeSO}_4$  but failed as it immediately broke down into  $\text{N}_3\text{H}$  and  $\text{Be}(\text{OH})_2$ .

- 1898; 13. Florence, W. Darstellung mikroskopischer Krystalle in Lothrohrperlen.

Ztschr. f. Kryst., 33, 180.

- 1898; 14. Goldschmidt, Dr. Hans. Ueber ein Neues Verfahren zur Darstellung von Metallen und Legierungen und von Korund, sowie zur Erzielung hoher Temperaturen.

Ztschr. angewandte Chem., 1898, 822.

Claims that Lebeau is wrong and that  $\text{BeO}$  is at least reduced in part by  $\text{Al}$  but comes in fine powder mixed with the slag. His proof is, however, simply that the mass grows dark and on ignition becomes white again and is far from convincing.

- 1898; 15. Liebermann, Louis. Verfahren sur Darstellung von Beryllium, D. R. P. 101326.  
Patent bl. 20, 193.  
Chem. Ztg., 23, 525.  
Ztschr. f. Elek., 5, 366.  
Chem. tech. Rep., 38, 120, 254.  
Electr. Chem. Ztg., 6, 81.  
Chem. Centrbl., 1899, I, 1096.  
Details of a patent of very doubtful value.
- 1898; 16. Liebermann, Louis. Verfahren zur Darstellung von Beryllium, D. R. P. 104632.  
Patent bl., 20, 816.  
Chem. Ztg., 23, 944.  
Ztschr. f. Elektr. Chem., 6, 284.  
Electro. Chem. Ztg., 6, 222.  
Ztschr. f. Elek., 5, 428.  
Chem. Tech. Rep., 38, 456.  
Chem. Centrbl., 1899, II, 1073.  
Patent of very doubtful value.
- 1898; 17. Roman, R. J. Beryllium Legierungen.  
Chem. Ztg., 22, 83.  
Claims priority over both Liebermann and Lebeau.
- 1898; 18. Moissan. Electrolytische Darstellung von Beryllium und seiner Legierungen und Darstellung von Beryllium Legierungen in Elektrischen Ofen.  
Chem. Ztg., 22, 650.  
Report of Lebeau's work before section on Electrochemistry of International Congress of Applied Chemistry, Vienna 1898.
- 1898; 19. Van Bemmelen, J. M. Die Absorption. Unsetzung der Krystallinischen Hydrate in amorphe Substanzen.  
Ztschr. f. anorg. Chem., 18, 126.  
Effects of heat on the "crystalline" and colloidal beryllium hydrate.
- 1898; 20. Franck, Leon. Studien über Aluminium als Reduktionsmittel.  
Chem. Ztg., 22, 244.

Claims that by heating  $\text{BeO}$  and  $\text{Al}$  in closed glass tube a reduction takes place, but gives no proof of the fact except that a gray mass, attacked by nitric acid, was formed.

Probably incorrect as Lebeau has shown.

- 1899; 1. Petersen, —. Note on preparation of pure beryllium oxide.

Chem. Ztg., 23, 439.

- 1899; 2. Meyer, Stefan. Ueber die Magnetischen Eigenschaften der Elemente (Beryllium).

Monatshefte, 20, 372.

Ann. der Phys. (Wied.), 68, 324.

J. Chem. Soc. (London), 76, 587.

Chem. Centrbl., 1899, 11, 163, 740.

Gives the magnetic susceptibility of beryllium as directly observed at  $15^\circ$  as  $+ 33.8 \times 10^{-6}$  in absolute units and atomic susceptibility for 1 gram per liter as  $+ .72 \times 10^{-6}$ .

- 1899; 3. Meyer, Stefan. Magnetisirungszahlen anorganische Verbindung.

Monatshefte, 20, 799.

Ann. der Phys. (Wied.), 69, 236.

Chem. Centrbl., 1900, 1, 5.

J. Chem. Soc. (London), 78, 7.

Determined the magnetic susceptibility of beryllium chloride, oxide, hydroxide, carbonate and sulphate.

- 1899; 4. Pozzie-Escot, M. E. Analyse microchimique.

Ann. de chim. anal., 4, 377.

Determines beryllium microscopically by crystals of the double oxalate of beryllium and potassium. Drawing of crystals given in original.

- 1899; 5. Havens, F. S. and Way, A. F. Separation of Iron from Chromium, Zirconium and Beryllium by the Action of Gaseous Hydrochloric Acid on the Oxides.

Amer. J. of Sci., (4) 8, 217.

J. Chem. Soc. (London), 78, 50.

Removes iron by hydrochloric acid gas mixed with a little chlorine at temperatures so low as  $200-300^\circ$ .

Higher temperatures act quicker—but if much iron is present some of the beryllium may be carried away mechanically.

- 1899; 6. Havens, F. S. and Way, A. F. Die Trennung des Eisens, von Chrom, Zircon und Beryllium durch die Einwirkung von gasförmiger Salzsäure auf die Oxyde. Ztschr. f. anorg. Chem., 21, 389.  
Review Amer. Chem. Research, 5, 102.  
Analyst., 25, 23.  
Same as 1899; 5 but separately transmitted.
- 1899; 7. Liebermann, L. Beryllium Legierungen. Chem. Ztg., 24, 43.  
Claims priority over Lebeau.
- 1899; 8. Austin, Martha. The double Ammonium Phosphates of Beryllium, Zinc and Cadmium in Analysis. Amer. J. of Sci., (4) 8, 206-216.  
Chem. Centrbl., 1899, II, 791.  
J. Chem. Soc. (London), 78, 49.  
Rev. Amer. Chem. Res., 5, 102.  
J. Soc. Chem. Ind., 19, 72.  
Shows that the precipitation of beryllium as ammonium beryllium phosphate and ignition to the pyrophosphate does not give uniform results.
- 1899; 9. Austin, Martha. Die Ammoniumdoppelposphate von Beryllium, Zinc and Cadmium in analytische Beziehung. Ztschr. anorg. Chem., 22, 207-220.  
Chem. Centrbl., 1899, II, 1032.  
Same as 1899; 8 but separately transmitted.
- 1899; 10. Ley, H. Studien über die hydrolytische Dissociation der Salzlosungen. Ztschr. phys. Chem., 30, II, 218.  
Chem. Centrbl., 1899, II, 1011.  
J. Chem. Soc. (London), 78, II, 67.  
Says basicity of  $\text{Be}(\text{OH})_2$  is eleven times as great as that of  $\text{Al}(\text{OH})_3$ . Found beryllium salts not so strongly

hydrolyzed as aluminum salts. Used inversion method. Worked on sulphate and chloride.

- 1899; 11. Lebeau, P. Recherches sur le glucinium et ses composés.

Ann. die chim. et de phys., (7) 16, 457-503.

Chem. Centrbl., 1899, I, 963.

J. Phys. Chem., 4, 222.

J. Chem. Soc. (London), 76, 554.

Ztschr. anorg. Chem., 21, 86.

Ztschr. f. Kryst., 34, 620.

This is a resumé of all of Lebeau's work on beryllium and is the best and most comprehensive article written on beryllium and its compounds.

- 1899; 12. Woulff, G. Optische Studien an pseudosymmetrischen Krystallen, Das Beryllium Sulfat.

Ztschr. f. Kryst., 17, 592.

Chem. Centrbl., 1900, II, 73.

$\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$  is strongly double refractive. The crystals are negative and uniaxial.

- 1899; 13. Rosenheim, A. u. Itzig, H. Ueber einige complexe Salz der Weinsäure und Apfelsäure und ihr spezifische Drehungsvermögen.

Berichte, 32, 3424.

Chem. Centrbl., 1900, I, 170.

Bull. soc. chim., (3) 24, 520.

J. Chem. Soc. (London), 78, 135.

J. Russ. Phys. and Chem. Soc., 32, II, 57.

Worked on the mono- and diberyllium tartrates of Rosenheim and Woge (1898; 4) to determine their molecular rotation and found that the introduction of beryllium into the molecule greatly increased the rotatory power whether right or left. Diberyllium tartrate showed a molecular rotatory power of  $225^\circ$ - $242^\circ$  not effected by dilution. Monoberyllium tartrate gave rotation of  $125^\circ$ .

Made double mallates with beryllium to correspond to the tartrates before described.

Addition of beryllium sulphate does not effect rotatory power of dextrose, or chlorosuccinic acid.

- 1899; 14. Amphola and Ulpiani. Sull'azione viduttrice dei batteri dinitrificanti.

Gazz. chim. Ital., 29, 49.

Bull. soc. chim., (3) 24, 363.

J. Chem. Soc. (London), 75, II, 444.

Studied the action of the denitrifying bacteria and found that *B. denitrificans* V. reduced beryllium nitrate and, in general, the more electro-positive the metal and the lower its atomic weight the more rapidly does denitrification take place.

- 1900; 1. Bruner, Ludwig. Ueber die Hydrolyse der Salzlösungen.

Ztschr. phys. Chem., 32, 133.

Chem. Centrbl., 1900, I, 532.

Bull. soc. chim., (3) 26, 599.

Gives figures for the hydrolysis of solutions of  $\text{BeCl}_2$ ,  $\text{Be}(\text{NO}_3)_2$ , and  $\text{BeSO}_4$ , compared with corresponding salts of iron and aluminum. The beryllium salts showed smaller degree of hydrolysis than either of the others.

- 1900; 2. Nielsen, R. A. Glühkörper aus Beryllerde.

Danish patent No. 4278.

- 1900; 3. Formánek, J. Nachweis der Metallsalze mittelst der Absorptionsspectralanalyse unter Verwendung von Alkanna.

Ztschr. anal. Chem., 39, 409.

If one treats Alkanna tincture with neutral beryllium chloride or nitrate, solution is red violet and fluoresces strong orange red. The absorption spectra consists of three distinct bands with position varying according to conditions.

- 1901; 1. Hartley, W. Noel. On the Quantitative Spectra of Beryllium.

Proc. Roy. Soc., 1902, 283-285.

Chem. News, 85, 25.



J. Chem. Soc. (London), 82, 237.

Chem. Ztg., 25, 1142.

Am. J. Sci., (4) 13, 156.

Solutions of beryllium salts of diminishing concentration examined spectroscopically and the gradual extinction of the several lines noted. Two lines  $\lambda$  3130.3 and 2478.1 are still visible when the concentration has fallen as low as .000001 per cent.

- 1901; 2. Urbain, G. and Lacombe, H. Sur un nouveau sel de glucinium volatile.

Comptes rend., 133, 874.

Chem. Centrbl., 1902, I, 97.

J. Phys. Chem., 6, 349.

Chem. News, 84, 304.

Chem. Ztg., 25, 1115.

J. Amer. Chem. Soc., 24, 201.

Ztschr. anorg. Chem., 33, 227.

Made  $\text{Be}_4\text{O}(\text{C}_2\text{H}_3\text{O}_2)_6$  by action of glacial acetic acid on dry acetate, excess of glacial acid being present. Melts at 283-284, distills under normal pressure at 330-331° and its vapor can be heated to 360° without decomposition. Density of vapor determined at boiling point of mercury 13.9. Not effected by solution in strongest acetic acid even if same is saturated with hydrochloric acid gas and heated in closed tube to 150°.

- 1901; 3. Wells, H. L. Generalizations on Double Halogen Salts.

Amer. Chem. Jour., 26, 390.

Chem. Centrbl., 1901, II, 1327.

Includes  $2\text{KF} \cdot \text{BeF}_2$ ,  $\text{KF} \cdot \text{BeF}_2$  and  $2\text{KCl} \cdot \text{BeCl}_2$  in his list of double halides.

- 1901; 4. Friedel, G. Sur un silicate de lithium crystallize.

Bull. soc. franc. de min., 24, 141.

Bull. soc. chim., (3) 25, 1008.

Chem. Centrbl., 1901, II, 88.

Sought to obtain some mixed crystals of  $\text{Li}_2\text{SiO}_3$  and  $\text{Be}_2\text{SiO}_4$  and succeeded in doing so. Claimed an ex-

ample of isomorphism similar to that between albite and anorthite.

- 1901; 5. Factor. Ueber die Einwendung des Natrium thiosulphate auf einige Metallsalze.

Chem. Centrbl., 1901, II, 879, from

Pharm. Post, 34, 485.

J. Chem. Soc. (London), 82, II, 25.

Claimed  $\text{BeS}_2\text{O}_3 \cdot 11\text{H}_2\text{O}$ .

- 1902; 1. Wyruboff, G. Sur quelques oxalates de glucine.

Bull. soc. franc. de min., 25, 71.

Chem. Centrbl., 1902, II, 631.

Again makes claims for the completely disproved theory of trivalent beryllium. Made the normal oxalate  $\text{BeC}_2\text{O}_4 \cdot 3\text{H}_2\text{O}$  and gives crystal measurements. Made also double oxalates of beryllium with potassium, rubidium, sodium and lithium.

- 1902; 2. Wyruboff, G. Sur la separation de la glucine.

Bull. soc. chim., (3) 27, 733.

Chem. Centrbl., 1902, II, 610.

J. Chem. Soc. (London), 82, 605.

Analyst., 27, 287.

Decomposes beryl with KOH, removes  $\text{SiO}_2$ , evaporates solution of chloride to small volume and precipitates beryllium as a double oxalate by means of  $\text{HKC}_2\text{O}_4$ .

- 1902; 3. Lacombe, H. Sur un type de composés du glucinium.

Comptes rend., 134, 772-74.

Chem. Centrbl., 1902, I, 1087.

Amer. J. Sci., (4) 13, 471.

J. Chem. Soc. (London), 82, I, 418.

Chem. News, 85, 215.

Chem. Ztg., 26, 373.

Made the basic formate, acetate, propionate, isobutyrate, butyrate, and isovalerianate, all of the same type as the basic acetate, *vis.*,  $\text{Be}_4\text{O}(\text{A})_6$ . All made by action of anhydrous acid in excess on the carbonate

and sublimation under diminished pressure. All attempts to saturate and obtain the normal salt failed. Formate, insoluble in all solvents. Solubility increases with increased molecular weight of acid radicle.

## CONSTANTS.

	M. P.	B. P. 760 mm.	B. P. 19 mm.
Basic formate, sublimes without fusion			
Basic acetate.....	283-284	330-331	sublimes
Basic propionate.....	119-120	339-341	221
Basic isobutyrate.....	76	336-337	216
Basic butyrate.....	liquid	.....	239
Basic isovalerianate.....	liquid	.....	254

- 1902; 4. Weinland, R. F. and Schlegelmilch. Ueber Doppelsalze des Jodtrichlorids mit Chloridin zweiwertigen Metalle.

Ztschr. f. anorg. Chem., 30, 140.

J. Chem. Soc. (London), 82, 315.

Prepared  $2\text{ICl}_3 \cdot \text{BeCl}_2 \cdot 8\text{H}_2\text{O}$  by passing chlorine into a hydrochloric acid solution of  $\text{BeCl}_2$  and iodine at  $10^\circ$ . Gold yellow, very hygroscopic needles. Very unstable.

- 1902; 5. Reubenbauer, Jacob. Ueber die Löslichkeit von Schwermetallhydraten in Natron.

Ztschr. anorg. Chem., 30, 334.

J. Chem. Soc. (London), 82, II, 396.

Found that  $\text{NaOH}$  dissolved  $\text{Be}(\text{OH})_2$  in proportion to the concentration of the  $\text{NaOH}$ .

- 1903; 1. Freundlich, H. Über das Ausfällen Kolloidaler Lösungen durch Elektrolyte.

Ztschr. f. phys. Chem., 44, 129.

Chem. Centrbl., 1903, II, 232.

Studied the action of  $\text{BeCl}_2$  and  $\text{BeSO}_4$  on colloidal  $\text{As}_2\text{S}_3$ .

- 1903; 2. Vogel, Fritz. Untersuchungen über Nitrite, (Beryllium nitrite).

Ztschr. anorg. Chem., 35, 385.

Chem. Centrbl., 1903, II, 327.

Could not obtain a nitrite of beryllium by precipitating

sulphate with barium nitrite. Precipitate immediately hydrolyzed and lost oxides of nitrogen. His precipitated hydroxide contained but a small amount of nitrogen  $\text{Be}:\text{NO}_2::1:0.15$ .

- 1903; 3. Renz, Carl. Ueber Verbindungen von Metalhaloiden mit organischen Basen.

Ztschr. anorg. Chem., 36, 100-118.

Chem. Centrbl., 1903, II, 578.

Succeeded in making but one compound of beryllium with the organic bases, *viz.*, Beryllium chloride quino-line,  $\text{BeCl}_2(\text{C}_9\text{H}_7\text{N}_2)_2 + \text{H}_2\text{O}$ .

- 1903; 4. Renz, Carl. Ueber die Löslichkeit der Hydroxide des Aluminiums, Berylliums und Indiums in Ammoniak und Aminbasen.

Berichte, 36, 2751-55.

Chem. Centrbl., 1903, II, 823.

Beryllium hydroxide is quite insoluble in methyl, ethyl, dimethyl and diethyl amine. This gives a quick and accurate and quantitative separation from aluminum. Solution of beryllium and aluminum are dissolved in dilute nitric acid, evaporated to remove acid, taken up in water, shaken up with large excess of ethyl-amine and the precipitated beryllium hydroxide carefully washed and aluminum determined in filtrate.

- 1903; 5. Van Oordt, G. Verfahren zur Reinabscheidung des Berylliums aus seinem Gemenge mit Aluminium und Eisen.

German Patent No. 155,466.

Chem. Centrbl., 1904, II, 1354.

Separates the basic acetate by its solubility in chloroform.

- 1904; 1. Pollok, James Holms. On the Extraction of Glucinum from Beryl.

Trans. Royal. Dublin Society, (2) 8, 139-152.

Extracted beryl by fusion with its own weight of sodium hydroxide in a salamander crucible. After separating silica from hydrochloric acid solution, he precipitated

with ammonia, filtered and dissolved the iron, aluminum and beryllium in hydrochloric acid and saturated with hydrochloric acid gas thereby separating the main quantity of aluminum. Separated from iron by ammonium carbonate and sulphide. Also in other experiments separated aluminum as alum in the ordinary way. Made perfectly free from aluminum by precipitating same with  $\text{HKF}_2$  in dilute  $\text{HF}$  solution. In strong solution some beryllium is also precipitated.

Basic carbonate finds formula approximately  $\text{BeCO}_3 \cdot 2\text{Be}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ . Carbonate is soluble to the extent of 58 grains in one liter saturated ammonium carbonate. Sulphate and chloride made in the usual manner, gives melting point of  $\text{BeCl}_2$  as about  $400^\circ$  and boiling point at about  $500^\circ$ . Made impure metallic beryllium by action of Na on anhydrous chloride in nickel crucible. Dark gray powder. Could not fuse at atmospheric pressure. In atmosphere of H it volatilized without fusion.

- 1904; 2. Haber, F. and Van Oordt, G. Ueber Berylliumverbindungen. I Mitteilung. Ueber Beryllium Hydroxide.

Ztschr. anorg. Chem., 38, 377-398.

Chem. Centrbl., 1904, I, 858.

A study of the hydroxide of beryllium convinced them that it existed in two modifications, first, when freshly precipitated which is readily acted upon by reagents and a second or older form, produced by standing or by boiling which is much less readily attacked.

- 1904; 3. Tanatar, S. Studies upon the Valency and the Atomic Weight of Beryllium.

J. Russ. Phys. and Chem. Soc., 36, 82-86.

Chem. Centrbl., 1904, I, 1192.

Repeats the work of Urbain and Lacombe (1901; 2) on the acetate and comes to the conclusion that Be is a tetravalent element with the atomic weight 18.2.

- 1904; 4. Haber, F. and Van Oordt. Berylliumverbindungen II Mitteilung.

Ztschr. anorg. Chem., 40, 465.

Chem. Centrbl., 1904, II, 688.

Separates beryllium from aluminum and iron by the solubility of its basic acetate in chloroform.

- 1904; 5. Parsons, Charles Lathrop. A Revision of the Atomic Weight of Beryllium.

Jour. Amer. Chem. Soc., 26, 721.

Ztschr. anorg. Chem., 40, 400.

Chem. News, 90, 61, 75.

Chem. Centrbl., 1904, II, 820.

Describes the preparation of pure material including the sulphate, chloride, acetyl-acetate and basic acetate. States that the supposed new element noted by Krüss and Moraht in beryllium compounds is a mixture of zinc and iron. Gives properties of the chloride, sulphate, acetyl-acetate and basic acetate. By the analysis of seven samples of beryllium acetyl-acetate and nine of basic acetate, obtained the atomic weight 9.113. Results on sulphate unsatisfactory and the method unreliable in the opinion of the author.

- 1904; 6. Neisch, A. C. A New Separation of Thorium from Cerium, Lanthanum and Didymium by Meta-nitrobenzoic acid.

J. Amer. Chem. Soc., 26, 781.

Chem. Centrbl., 1904, II, 848.

Meta nitrobenzoic acid does not precipitate beryllium.

- 1904; 7. Myers, Ralph E. Results obtained in Electrochemical Analysis by the Use of a Mercury Cathode.

J. Amer. Chem. Soc., 26, 1124.

Chem Centrbl., 1904, II, 1338.

Separation of beryllium from chromium and iron. By the use of a mercury cathode all the iron and chromium present in a slightly acid solution of the sulphates and beryllium sulphate can be deposited in the mercury, leaving pure beryllium sulphate behind.

- 1904; 8. Wetherel, E. W. An Attempt to Explain the Irregularities of the Atomic Weights of Beryllium, Argon and Tellurium.  
Chem. News, 90, 260.  
Chem. Centrbl., 1905, I, 7.
- 1904; 9. Pollok, James Holms. The Heat of Formation of Glucinium Chloride.  
J. Chem. Soc. (London), 85, 603.  
Pro. Chem. Soc. (London), 20, 61.  
Chem. Centrbl., 1904, I, 1243, 1593.  
Describes the extraction of the oxide from beryl. Formation and properties of anhydrous chloride. Melting point of chloride about  $400^{\circ}$ .  
Molecular heat of solution  $\text{BeCl}_2 = 44.5 \text{ K}^{\circ}$ .  
Molecular heat of solution  $\text{BeSO}_4 \cdot 4\text{H}_2\text{O} = 0.85 \text{ K}^{\circ}$ .  
Molecular heat of formation  $\text{BeCl}_2 = 155 \text{ K}^{\circ}$ .  
Prepared metallic beryllium by action of sodium on chloride and obtained an impure product. Says metal volatilizes without fusion at ordinary pressure.
- 1904; 10. Parsons, Charles Lathrop. Equilibrium in the System Beryllium Oxide, Sulphuric Anhydride and Water.  
J. Amer. Chem. Soc., 26, 1433.  
Ztschr. anorg. Chem., 42, 250.  
Chem. Centrbl., 1905, I, 2.  
Made a study of the various published sulphates of beryllium including the so-called basic sulphates and concludes that the only definite sulphates are the tetrahydrate and dihydrate, and by the application of phase rule considerations, the basic sulphates are shown to be either the hydroxide or a solid solution of the sulphate in the hydroxide.
- 1904; 11. Parsons, Charles Lathrop. "Beryllium" or "Glucinium" Science, Dec. 9, 1904.  
Chem. News, 91, 75.  
Discussion of the proper name for element. Prefers beryllium.

- 1904; 12. Pollok, James Holms. The Composition of Beryl.  
Proc. Chem. Soc. (London), 20, 189.  
J. Chem. Soc. (London), 85, 1630-37.  
Chem. Centrbl., 1905, I, 556.  
By fractional sublimation of the chloride of beryllium, he obtained chlorides which on analysis yield equivalents for Be all the way from 4.77-18.74 and concluded the beryllium is really a mixture of two elements.  
Examined the oxides from the two chlorides spectroscopically.
- 1905; 1. Howe, James Lewis. "Glucinium" or "Beryllium."  
Science, Feb. 17, 1905.  
Chem. News, 91, 123.  
Reply to 1904; 10, Prefers glucinium.
- 1905; 2. Parsons, Charles Lathrop. "Beryllium" or "Glucinium."  
Science, Jan. 6, 1905.  
Chem. News, 91, 123.  
Chem. Centrbl., 1905, I, 1129.  
Reply to Howe 1905; 1.
- 1905; 4. Parsons, Charles Lathrop. On the Complexity of Beryllium.  
J. Amer. Chem. Soc., 27, 233.  
Chem. News, 91, 92.  
Chem. Centrbl., 1905, I, 995, 1306.  
Discusses the work of Pollok (1905, 4) and claims that his results are easily explained by the action of water on beryllium chloride and that sufficient precautions were not taken to guard against its presence.
- 1905; 5. Parsons, Charles Lathrop. Note on the Atomic Weight of Carbon and Beryllium.  
J. Amer. Chem. Soc., 27, 1204.  
Ztschr. anorg. Chem., 46, 215.  
Chem. Centrbl., 1905, II, 956, 1155.  
Obtains new figures from his previously published analyse for the atomic weight of beryllium. By an algebraic calculation both the atomic weight of carbon



and beryllium are independently obtained from the previously published figures.

Atomic weight Be = 9.112.

Atomic weight C = 12.007.

- 1905; 6. Kahlbaum, G. W. A. and Sturm, E. Ueber die Ver-  
andlichkeit des Spezifischen Gewichtes.

Ztschr. anorg. Chem., 46, 237.

Chem. Centrbl., 1905, II, 1068.

Compares beryllium to other members of the same group and gives reasons why it was not used in his research.

- 1905; 7. Levi-Malvano, Mario. Gli idrati del solfato di berillio.  
Atti. R. Accad. die Lincei, Roma, (5) 14, II, 502-10.

Ztschr. anorg. Chem., 48, 446.

Chem. Centrbl., 1906, I, 321, 1223.

Describes a sulphate hexahydrate of beryllium which he makes from supersaturated solution and states that it yields a blue oxide on ignition. Gives solubility curves of the hexahydrate and also the tetrahydrate. Concludes that a sulphate monohydrate and anhydrous sulphate both exist.

- 1906; 1. Parsons, Charles L. and Robinson, W. O. Equilibrium in the System Beryllium Oxide, Oxalic Anhydride and Water.

J. Amer. Chem. Soc., 28, 555.

Ztschr. anorg. Chem., 49, 178.

Chem. Centrbl., 1906, II, 8.

Made a study of the oxalates of beryllium in the same manner as the previous work, (1904, 10) on the sulphate and concludes that an acid oxalate does not exist and the oxalates of beryllium alone are the mono and trihydrates. Further that all of the so-called basic oxalates are in reality solid solutions approaching the hydroxide in composition. Give a list and general discussion of basic beryllium compounds and state their belief that no definite basic compounds claimed to have been formed in presence of water have any real exist-

ence as chemical compounds. Cut and drawing of crystals of the trihydrated oxalate. Purification of material by recrystallization of the basic acetate from glacial acetic acid.

- 1906; 2. Parsons, Charles L. and Barnes, Stuart K. The Separation and Estimation of Beryllium.

Science, 24, 240.

J. Amer. Chem. Soc., 28, 1589.

Chem. Centrbl., 1907, I, 67.

Ztschr. f. anal. Chem., 46, 292.

Chem. Centrbl., 1907, II, 96.

J. Chem. Soc., 92, 52.

Chemical Abstracts, 1, 27.

Beryllium is separated from aluminum and iron by the complete solubility of its hydroxide in a hot saturated solution of acid sodium carbonate—ferric hydroxide and aluminum hydroxide being completely insoluble. Double precipitation is essential. Beryllium hydroxide must be washed with water containing an electrolyte in solution, for when pure it rapidly washes through the filter in a colloidal condition.

- 1906; 3. Parsons, Charles L. and Robinson, W. O. The Basic Solutions of Beryllium Sulphate.

Science, 24, 202.

Freezing-point determinations, on both dilute and concentrated solutions, show that, per mol of  $\text{SO}_4$ , any increase in basic ratio over the normal salt raises the freezing-point. The osmotic effect of the sulphate is, therefore, always decreased by dissolving in it its own hydroxide. The electrical conductivity of the basic solutions is less than that of normal solutions containing the same amount of  $\text{SO}_4$ . Migration experiments show that beryllium forms no part of the anion. The basic solutions are not precipitated by crystalloids; but on dialysis hydroxide is left on the membrane, and the dialyzed solution has a lower basic ratio.

- 1906; 4. Parsons, Charles L. and Roberts Edwin J. Beryllium Carbonate.

Science, 24, 39.

Normal beryllium carbonate can not be made at ordinary pressures in contact with water.  $\text{BeCO}_3 + 4\text{H}_2\text{O}$  described by Klatzo does not exist, and attempts to make it by his method yield only slightly carbonated hydroxide. Basic beryllium carbonate appears to have no definite composition and can be almost completely converted into the hydroxide by boiling in water. All attempts to increase the proportion of the  $\text{CO}_2$  components over the proportion  $2\text{Be}(\text{OH})_2 \cdot \text{BeCO}_3$  failed, although  $\text{CO}_2$  was passed for three months through the basic carbonate under slightly increased pressure. The basic carbonates described in literature must have contained at least one or two per cent. of the carbonate used as a solvent or precipitant.

- 1906; 5. Parsons, Charles L. and Fuller, Carl T. Further Study of the Sulphates of Beryllium.

Science, 24, 202.

Crystals were obtained from solutions with a ratio as high as  $3\text{BeO}/2\text{SO}_4$ . These crystals are in every case the normal tetrahydrate, and by their separation the mother-liquors are rendered more basic. Repeated attempts to obtain the hexa-hydrate described by Levi-Malvano (*Ztschr. anorg. Chemie*, 48, 446.) have resulted in failure. Although the conditions described by that author were faithfully followed and other methods used, the tetrahydrate invariably separated.

- 1906; 6. Van Oordt, G. Verfahren Zur Überführung von Beryllium Hydroxide in einen nicht nur für Alkali, sondern auch für Säure schwerlöslichen bzw. unlöslichen Zustand.

Kl. Patent, 12m. No. 165,488 of Sept. 12, 1903.

Chem. Centrbl., 1906, I, 108.

A patent on the principle published by Haber and Van

Oordt (1904; 2) which he claims to apply to a method of separation.

- 1906; 7. Brau, F. and Van Oordt, G. Verfahren Zur Trennung der Beryllerde von Thonerde und eventuell Eisen. Kl. Patent, 12m. No. 175,452.  
Chem. Centrbl., 1906, II, 1370.  
Chemical Abstracts, 1, 2316, 2514.

A patent for the separation of beryllium on the principle described in 1906; 2.

- 1906; 8. Glassmann, B. Zur quantitativen Trennung des Beryllium von Aluminium.  
Berichte, 39, 3366-67.  
Chem. Centrbl., 1906, II, 1584.  
Chem. Abs., 1, 151.

Claims to separate by essentially the same method as proposed by Berthier (1843; 2) and discarded as early as 1844 (1844; 1) by Böttinger.

- 1906; 9. Glassmann, B. Zur quantitativen Bestimmung des Berylliums.  
Berichte, 39, 3368-69.  
Chem. Centrbl., 1906, II, 1584.  
Chem. Abs., 1, 152.

Precipitates beryllium hydroxide from neutral solution of pure salts by a mixture of potassium iodide and iodate after previous removal of iron and alumina. Has the advantage over  $\text{NH}_4\text{OH}$  that the precipitate is easily washed.

- 1906; 10. Tanatar, S. Über die Wertigkeit und das Atomgewichte des Berylliums (Spezifische Wärme des Berylliums oxyds).

Jour. Russ. Phys. Chem. Ges., 38, 850-54.

Chem. Centrbl, 1906, II, 1807.

Determines the specific heat of the oxide at 100-117° as .2898 and calculates therefrom an abnormally low specific heat for the metal, and argues therefrom for the tetravalency of the element exactly as the well known

low specific heat of the element was formerly used as an argument for its trivalency.

- 1906; 11. Olmstead, Charles M. Die Bandenspektren nahe verwandte Verbindungen.

Zeit. f. wiss. Photographie, Photophysic u. Photochemie, 4, 255-91.

Chem. Centrbl., 1907, I, 147.

Studied the band spectra of Ba, Sr, Ca and Mg. Could obtain no spectrum from beryllium chloride and thinks temperature was probably not high enough for this purpose.

- 1906; 12. Friedheim, Carl. Zur quantitativen Trennung des Berylliums und Aluminiums.

Berichte, 39, 3868-69.

Chem. Centrbl., 1907, I, 191.

Chem. Abs., 1, 277.

Calls attention to the fact that Glassmann's (1906; 8) supposed new method had been proposed much earlier and tried by several authors.

- 1906; 13. Parsons, Charles L. Beryllium Nitrate.

Science, 25, 402.

Prepares  $\text{Be}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  by crystallizing from strong nitric acid. Crystals very deliquescent, lose their  $\text{N}_2\text{O}_5$  easily, are stable only in strong nitric acid or in air saturated with its vapor, melt in their own water of crystallization at 60.5, soluble in alcohol and in acetone.

- 1907; 1. Glassmann, B. Über die Konstitution der fettsauren Salze des Berylliums und sur Wertigkeit des letztern.

Chem. Ztg., 31, 8-9.

Chem. Centrbl., 1907, I, 707.

J. Chem. Soc., 92, 109.

Chem. Abs., 1, 701.

Criticises the conclusions of Tanatar (1904; 3) that the basic beryllium salts of the fatty acid series show beryllium to be tetravalent. Explains valency on divalency basis.

- 1907; 2. Kühne, K. A. Verfahren zur Darstellung von Metallen, u. s. w.  
Patent Kl 40a, No. 179,403.  
Chem. Centrbl., 1907, I, 1474.  
Proposes to separate Be, Bo, Si, etc., by Goldschmidt's aluminum method by adding them to the mixture in the form of chlorates or perchlorates.
- 1907; 3. Parsons, Charles L. The Vagaries of Beryllium.  
Science, 26, 569-74.  
Chem. News, 96, 131.  
Address of the chairman of the Inorganic Section, Toronto meeting, American Chemical Society.
- 1907; 4. Glassmann, B. Zur Kenntniss der Chromate des Berylliums.  
Berichte, 40, 2602-4.  
Chem. Centrbl., 1907, II, 375.  
Chem. Abs., I, 2352.  
Claims to have made neutral chromate,  $\text{BeCrO}_4 \cdot \text{H}_2\text{O}$  by "neutralizing" a concentrated water solution of chromic acid with basic beryllium carbonate and evaporating. (Obtained reddish yellow monoclinic crystals which are decomposed by water with separation of a basic chromate, to which he gives the formula,  $\text{BeCrO}_4 \cdot 6\text{Be}(\text{OH})_2$  or by precipitation of ammonium chromate with  $\text{BeSO}_4$  solution.  
(Other investigators who have tried to produce the chromate in this manner have obtained only indefinite basic mixtures.)
- 1907; 5 Steinmetz, Hermann. Über Beryllium Acetate.  
Ztschr. f. anorg. Chem., 54, 217-22.  
Chem. Centrbl., 1907, II, 528.  
J. Chem. Soc., 92, 673.  
Chem. Abs., I, 2672.  
Basic beryllium acetate gives octahedral crystals, from organic solvents which on sublimation yield doubly refracting leaves and prisms. It forms an unstable compound,  $\text{Be}_4\text{O}(\text{Ac})_6 \cdot 3\text{C}_5\text{H}_5\text{N}$  in cold pyridine. He made

normal beryllium acetate,  $\text{Be}(\text{C}_2\text{H}_3\text{O}_2)_2$  for the first time by heating equal parts of basic acetate and glacial acetic acid with 5-6 parts acetic anhydride for 2 hours in a sealed tube at  $140^\circ$ . It forms double refracting small leaflets which are insoluble in water, alcohol, ether and organic solvents. They are hydrolyzed by continued boiling in water, melt with decomposition at  $300^\circ$  and yielding a sublimate of the basic acetate.

- 1907; 6. Glassmann, B. Ein Beitrage zur Bivalenz des Berylliums. Das Beryllumpikrat.

Berichte, 40, 3059-60.

Chem. Centrbl., 1907, II, 777.

J. Chem. Soc., 92, 695.

Chem. Abs., I, 2539.

By "neutralizing" a water solution of picric acid with basic beryllium carbonate, obtained a substance in yellow scales to which he gave the formulas  $\text{Be}(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2 \cdot 3\text{H}_2\text{O}$  by calculation from its  $\text{BeO}$  content. By treating with ether he states it loses one molecule of water. On drying all the water is removed and the residue was soluble in alcohol, acetone, and pyridine but difficultly soluble in ether. In acetophenon it gave a freezing point lowering giving a molecular weight of 465. By the action of water it is hydrolyzed and yields a basic mass to which Glassmaun gives the formula  $\text{Be}(\text{C}_6\text{H}_2\text{O}_7\text{N}_3)_2 \cdot 20\text{Be}(\text{OH})_2$ .

- 1907; 7. Bourion, F. Action du chlor et du chlorur de soufre sur quelques oxydes.

Comptes rend., 145, 62-64.

Chem. Centrbl., 1907, II, 880.

Chem. Abs., I, 2988.

Beryllium oxide is converted into  $\text{BeCl}_2$  by the action of a stream of  $\text{Cl}$  and  $\text{S}_2\text{Cl}_2$  at a red heat.

- 1907; 8. Nicolardot, P. Glucinium ou Beryllium.

Bull. soc. chim., (4) I, 675-81.

Chem. Centrbl., 1907, II, 1152.

Argues in favor of the French usage.

- 1907; 9. Stein, Gerh. Über die Darstellung einiger Silicate.  
Ztschr. f. anorg. Chem., **55**, 159-74.  
Chem. Centrbl., **1907**, II, 1218.

Obtained a meta silicate  $\text{BeSiO}_3$  with a density 2.35 and an orthosilicate with density 2.46 by fusing the oxide with  $\text{SiO}_2$  in a carbon tube oven electrically heated to above  $2000^\circ$ . Melting point of each about  $2000^\circ$ .

- 1907; 10. Parsons, C. L., Robinson, W. O. and Fuller, C. T.  
The Soluble Basic Sulphates of Beryllium.  
Journal of Physical Chemistry, **11**, 655.  
Chem. Centrbl., **1908**, I.  
J. Chem. Soc., **94**, 105.

It is shown that a solution of beryllium hydroxide in a solution of beryllium sulphate raises the freezing point of the latter and lowers its conductivity. The solutions obtained are not colloidal nor does the beryllium enter into a complex anion as is shown to be the case when a berylonate is present.

- 1907; 11. Parsons, Charles L. Solution in a Dissolved Solid.  
Jour. of Phys. Chem., **11**, 660.  
Chem. Centrbl., **1908**, I.  
J. Chem. Soc., **94**, 89.

An explanation presented with several analogous experiments to account for the solubility of  $\text{Be}(\text{OH})_2$  in solutions of beryllium salts.

- 1907; 12. Tanatar, S. and Kurowski, E. K. Über einige Salze des Berylliums und Zirkoniums.  
J. Russ. Phys. Chem. Soc., **39**, 936-43.  
Chem. Centrbl., **1908**, I, 102.  
J. Chem. Soc., **92**, 888.

Adhering to his previously announced belief in the tetravalency of beryllium, he claims to have made salts of several organic acids by saturating their water solutions with basic beryllium carbonate. By evaporating these solutions and analyzing the solid obtained for  $\text{BeO}$  only, he calculates the formulas given below. Formate,  $\text{Be}(\text{CHO}_2)_2$ , Basic Formate,  $\text{Be}_4\text{O}(\text{CHO}_2)_6$ .



Crotonate,  $\text{Be}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_4$ , soluble in benzene and alcohol, crystals, volatile with decomposition. Gives normal molecular weight in benzene.

Isocrotonate, much the same as the crotonate.

Laevalinate,  $\text{Be}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_4$ , soluble in water, alcohol and benzene and freezing point in benzene corresponds to above.

Succinate,  $\text{Be}_4\text{O}(\text{C}_4\text{H}_4\text{O}_4)_4$ , white powder insoluble in benzene and alcohol.

Maleate and Fumarate,  $\text{BeC}_4\text{H}_2\text{O}_4$ .

Citraconate,  $\text{BeC}_5\text{H}_4\text{O}_4$ .

Also obtained derivatives of the basic butyrate and propionate as follows by treating them with acetyl chloride.

$\text{Be}_4\text{O}(\text{C}_4\text{H}_7\text{O}_2)_4 \cdot (\text{C}_2\text{H}_3\text{O}_2)_2$ , melting point  $15^\circ$ , boiling point  $351^\circ$ , soluble in benzene and ether.

$\text{Be}_4\text{O}(\text{C}_4\text{H}_5\text{O}_2)_3 \cdot (\text{C}_2\text{H}_3\text{O}_2)_3$ , melting point  $127^\circ$ , boiling point  $330^\circ$  without decomposition. Soluble in benzene and ether.

(Note. While the acetyl derivatives of the well known butyrate and propionate can probably be depended upon, the salts enumerated above need confirmation as it is a perfectly simple matter to get residues of this character with organic acids which will calculate almost any formula if their content of beryllium oxide is the only criterion. It should also be remembered that the addition of basic beryllium carbonate to any organic acid beyond the amount necessary to form the normal salt causes solutions of the substance formed to have a higher freezing point than the solution of the normal salt, which might easily account for the molecular weights calculated within the limits of error of Tanatar's experiments. Certainly neither the normal formate nor the basic formate of Lacombe can be prepared in the presence of water, and many attempts at preparing the succinates by the compiler of this bibliography have resulted only in indefinite mixtures of variable com-

position, one of which could easily have been found to meet the description of Tanatar's succinate and still have been simply a solid solution.)

- 1907; 13. Tanatar, S. M. and Kurowski, E. K. Beryllium and Zirconium Benzoates.

J. Russ. Phys. Chem. Soc., 1907, 39, 1630.

J. Chem. Soc. (London), 94, 166.

By action of water solution of sodium benzoate on a solution of beryllium acetate, he obtained a white amorphous substance, soluble in benzene and acetone which from its  $\text{BeO}$  content he assumes to be a benzoate of type  $\text{Be}_4\text{O}(\text{Ac})_6$  and claims it is similar to a zirconium benzoate, similarly obtained as a further argument for the tetravalency of beryllium.

- 1907; 14. Raikow, P. Weitere Untersuchungen über die Einwirkung der Kohlensäure auf die Hydrate der Metalle. Chem Ztg., 31, 55, 87.

Chem. Centrbl., 1907, 1, 695.

Chem. Abstracts, 1, 825, 967.

Beryllium forms no carbonate unless possibly a basic carbonate of composition  $\text{BeCO}_3 \cdot 3\text{Be}(\text{OH})_2$ .

- 1907; 15. Biltz, W. and Zimmermann, Fr. Ueber die Einwirkung von Silbernitrat and Mercurinitrat auf einige Anorganische Hydroxide.

Berichte, 40, 4979-84.

Chem. Centrbl., 1908, I, 444.

Silver nitrate is without effect on beryllium hydroxide. Mercuric nitrate solution is colored yellowish red by the neutral hydroxide. Authors conclude from comparison that  $\text{Be}(\text{OH})_2$  has an ion solubility of the high order of  $10^{-5}$ .

- 1908; 1. Glassmann, B. Zur Konstitution der fettsauren Salze des Berylliums, über einige Neue Beryllium orthosalze und über Salze organische Orthosauren anderer Elements.

Berichte, 41, 33.

Argues for his constitutional formulas for organic

beryllium compounds as against Tanatar. Also offers the following new salts all of which need confirmation by equilibrium experiments before being accepted (See note 1907; 13):

Lactate,  $\text{Be}_2\text{O}(\text{C}_3\text{H}_5\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , crystals, soluble in water;

Glycolate,  $\text{Be}_2\text{O}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ , crystals, soluble in water;

Trichloracetate,  $\text{Be}_2\text{O}(\text{C}_2\text{Cl}_3\text{O}_2)_2$ , glassy mass;

Ethylglycolate,  $\text{Be}_2\text{O}(\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{H}_2\text{O}$ ;

Phenylglycolate,  $\text{Be}_2\text{O}(\text{C}_6\text{H}_5\text{C}_2\text{H}_3\text{O}_2)_2$ ;

Chloropropionate,  $\text{Be}_2\text{O}(\text{C}_3\text{H}_4\text{ClO}_2)_2 \cdot \text{H}_2\text{O}$ ;

Salicylate,  $\text{Be}_2\text{O}(\text{C}_7\text{H}_5\text{O}_2)_2$ ;

Cyanacetate,  $\text{Be}_4\text{O}(\text{C}_2\text{H}_2\text{CNO}_2)_6$ , glassy mass.

Dichloracetate,  $\text{Be}_4\text{O}(\text{C}_2\text{HCl}_2\text{O}_2)_6$ , crystalline;

Monobromacetate,  $\text{Be}_4\text{O}(\text{C}_2\text{H}_2\text{BrO}_2)_6$ , crystalline.

Monochloracetate,  $\text{Be}_4\text{O}(\text{C}_2\text{H}_2\text{ClO}_2)_6$ , crystalline

Monobrompropionate,  $\text{Be}_4\text{O}(\text{C}_3\text{H}_4\text{BrO}_2)_6$ , crystalline

All the above "salts" are easily soluble in water, in soluble in benzene and chloroform and all non-volatile. All were made by "neutralizing" the water solution of the acid with basic beryllium carbonate and evaporating. The composition of the solid residue was inferred from the content of  $\text{BeO}$  found, adding water of crystallization where necessary to make the calculated quantity of oxide agree therewith.

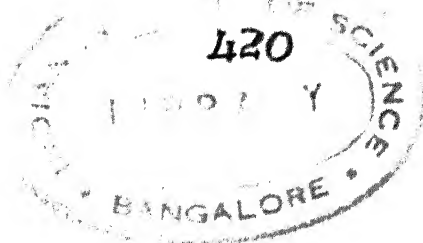
- 1908; 2. Noyes, A. A., Bray, W. C. and Spear, E. B. A System of Qualitative Analysis for the Common Elements. Part III Analysis of the Aluminium and Iron Groups including Beryllium, Uranium, Vanadium, Titanium, Zirconium and Thallium.

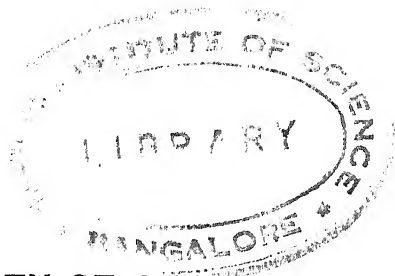
J. Amer. Chem. Soc., 30, 481

- 1908; 3. Cameron, F. K. and Robinson, W. O. The Action of Carbon Dioxide under Pressure upon a Few Metal Hydroxides at  $0^\circ\text{C}$ .

Jour. Phys. Chem., 12, 562.

The authors show that no definite carbonate of beryllium exists.





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